Waterloo Research Institute

Screening Program on Short Residence Time Pyrolysis of Coal

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Summary

All the objectives proposed in the original contract and the extension have been met, with reasonably definitive results in most cases for the eight coals investigated (one lignite, three sub-bituminous and four bituminous).

1. The fluid bed flash pyrol[illegible]is process exhibits an optimum temperature for maximum liquid y[illegible]. This temperature is from 600°-650° for low rank coals and 650°-700°[illegible]or higher rank coals. The maximum tar yield for Canadian bituminous coals can be predicted from the CSIRO correlation of parent coal H/C ratio vs maximum tar yield. Tar yields from lower rank coals are not yet predictable, and are not related to the volatile yield of a proximate analysis.

2. The tar and char products from low rank coals show a decreasing atomic H/C ratio as temperature increases. The H/C ratios for bituminous coal tars and chars remain reasonably constant with temperature.

3. For both low rank and high rank coals the shortest residence time gave the highest liquid yields (0.2 to 0.45 seconds).

4. The minimum particle size for good liquid yields from fluidized beds appears to be about 100 μm. However, this will be a function of reactor configuration, operating mode and heat transfer capabilities.

5. Accumulation of char in the reactor does not affect liquid yields providing the char is not activated at high temperatures (above 900°C). The use of a CO_2 atmosphere does not appear to improve liquid yields for a coal previously exposed to CO_2. However, a fresh, unoxidized coal might show some effect - this has yet to be determined.

6. The use of a hydrogen atmosphere and a Co-Mo deoxygenation-hydrogenation catalyst as the fluid bed material did not improve tar yields for lower rank coals. However, catalytic effects were evident, so that a different choice of catalyst might prove to be beneficial.

7. Quenching of the reaction products with a flow of cold gas did not improve liquid yields in this reactor. The reasons are not clear, but may be due to higher gas velocities in the reactor.

8. Acid washing of a lignite to remove cations associated with the organic matter, followed by pyrolysis, gave a dramatic increase in maximum tar yield - about 50%. The acid washed lignite gives a tar yield in agreement with that predicted from CSIRO and U.S. results for acid washed lignites or brown coals.

9. Pre-oxidation of a strongly caking bituminous coal prevents agglomeration and caking in the fluidized bed. Without such pretreatment, operating problems due to caking of the bed solids may arise. However, pre-oxidation of the coal also causes a significant decrease in tar yield. Some optimum level of treatment should exist.

10. In general, Canadian coals, expecially those from Western Canada, have low H/C ratios compared to coals of similar rank from other sources. Low H/C ratios can be correlated generally to lower tar yields. The highest tar yields were obtained from high volatile bituminous coal, (16-20%), or from acid washed lignite (12-14%). The lowest tar yields were obtained from low volatile bituminous coal, or from high ash sub-bituminous coals (5-7%). The range of tar yields from lignite, sub-bituminous coals or medium volatile bituminous coals is from 10-14% (all yields maf).

11. Chars produced in the pyrolysis process, particularly those formed at the lower temperatures, are very reactive. There is strong evidence that they rapidly adsorb oxygen and water from the air even on short exposure.

12. Future studies on pyrolysis of coals should use dry feeds, and chars should be kept in a dry inert atmosphere as much as possible, if good material balances and good analytical results are desired.

13. The fluidized bed reactor appears to be a very suitable device for the pyrolysis of lignite or sub-bituminous coals. No operating problems were encountered in the bench scale unit and product yields were about the same as those obtained by others. The "blow-through" method of operation used in the Waterloo Flash Pyrolysis process for biomass appears to be feasible also for low rank coals, so that transport of heat carrying sand is not necessary and a single fluidized reactor with an independent heat source can be used.

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The author is aware that he is to a large degree only the reporter for those who actually carried out the work, and he would like to express his appreciation to his fellow workers - to Jan Piskorz, for his supervision of all the experimental investigations and for his contributions to our understanding of the pyrolysis process, to Mike Ebert, who carried out most of the experimental measurements reported, and to Dave Kibble who also contributed to the experimental results.

Screening Program on Short Residence Time Pyrolysis of Coal

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INTRODUCTION

Chronology

Work on coal pyrolysis was initiated at the University of Waterloo in 1979 using a small bench scale fluidized bed apparatus patterned after that developed by CSIRO (Tyler 1979). During the initial work carried out (Scott, 1980) a somewhat larger scale reactor was developed than that used by Tyler - 15 gms/hr through put rather than 1-3 gms/hr. This larger scale was made possible by the development of a new entrained flow feeder which allowed feed rates of 5-100 gms/hr with a reproducibility of ± 5% (Scott and Piskorz, 1982). In this preliminary work, the methodology and procedures were developed for the bench scale mini-fluidized bed apparatus, and a series of pyrolysis tests were done on Alberta Forestburg sub-bituminous coal which indicated that yields of liquids comparable to those obtained by others could be realized.

In June, 1981, a new program was initiated to evaluate the short residence time pyrolysis of coal at atmospheric pressure with the primary objective of determining conditions for optimum yields of liquids from a sub-bituminous coal (Scott, 1982). During this work, covering the period to June 1, 1982, the bench scale fluidized bed method was improved so that better material balances were obtained, and a small stainless steel reactor was developed in place of the earlier quartz version. In fact, three coals were tested for pyrolysis behaviours, two Alberta sub-bituminous coals and a Nova Scotia bituminous coal.

Results from this work were sufficiently encouraging that a further program was planned for 1982/83 and funding was received on October 1, 1982. It is the results from this program, including a minor extension to March 31, 1984, which will be the subject of this report.

A part of the two earlier reports has been a state-of-the-art review of coal pyrolysis research activities, particularly in North America and the Pacific. This report will not include such a review, inasmuch as it was not one of the objectives of the study.

Summary of Early Work

The previous study reported that yields of 10% - 12% (max) of hydrocarbon liquids could be obtained from Alberta Forestburg or Highvale (Wabamun) coal at optimum conditions of 650°C, one atmosphere absolute pressure in a nitrogen atmosphere and about 0.44 secs. apparent gas residence time. Both these coals are sub-bituminous, low to medium volatile in rank. Additional pyrolysis tests done on a Devco coal (high volatile bituminous caking coal) indicated that oil yields of 17% - 21% max could be obtained at temperatures from 650°-750°C and about 0.5 sec. apparent residence time. However, operating problems with the fluidized bed were also encountered due to the caking behaviour of the coal.

Additional tests using the sub-bituminous coals showed that a CO_2 atmosphere seemed to have little effect in increasing liquid yields, contrary to literature reports. A hydrogen atmosphere reduced liquid yields and increased gas yields.

The major analytical problems were found to be in the accurate determination of water, and in obtaining good results for the amounts of highly volatile hydrocarbon liquids produced. However, tar yields, when normalized, appeared to agree well with those of other workers reported in the literature for coals having similar H/C ratios.

OBJECTIVES OF PRESENT WORK

The primary objective of the work undertaken during this research program is to determine the pyrolysis conditions for an atmospheric pressure fluidized bed process which result in a maximum yield of liquid products. Initial studies suggest that these optimum conditions will be different for different coals. Further, some coals are readily processed in a fluidized bed reactor, while others appear to be likely to cause operating problems if not handled correctly. In addition, reports in the literature have suggested various pre-treatments for coal which may have the effect of increasing liquid yields or minimizing operating problems. The objectives of the present work, therefore, were to screen a number of Canadian coals of widely varying character in order to determine the optimum conditions for pyrolysis, and the effects of some pre-treatments or alternative processing methods on liquid yields.

Specific objectives originally planned are listed as follows:

(a) To determine for a number of coals, preferably three bituminous, one lignite and two sub-bituminous, the liquid yields as a function of temperature from 450° - 750°C at "standard" conditions.

(b) For a coal of each rank, determine the effect of particle size.

(c) For a low rank and high rank coal, to determine the effect of vapour residence time insofar as this could be varied in a fluidized bed reactor.

(d) For a coal of each rank, to test the effect on liquid yields of using a carbon dioxide or a hydrogen atmosphere.

(e) Using a sub-bituminous coal and a hydrogen atmosphere, to investigate the effect of replacing the sand in the fluidized bed with a Co-Mo catalyst.

(f) To investigate the effect of pre-oxidation of a caking coal on its performance in a fluid bed and the effect of this pre-oxidation on liquid yields.

(g) To investigate the effect of acid washing of a lignite coal on liquid yields.

(h) To investigate insofar as was possible the effect on liquid yields of char accumulation in the fluid bed, that is, of the sand/char ratio in the reactor.

The latter two objectives were the subject of the contract extension to March 31, 1984, mentioned previously.

All of the above objectives have been accomplished as planned, with reasonably definitive results in most cases. However, data from runs using caking coals is not as extensive as with lower rank coals, because of the operating difficulties caused by these coals.

APPARATUS AND PROCEDURES

During the course of the present investigations a number of modifications to apparatus and to procedures were tried in order to solve operating or analytical problems. Some of these were successful, some were not.

Water analysis was carried out in earlier work by taking a hot (150°C) sample from the reactor free board space and analysing this in a Carle gas chromatograph. This method often gave results with a high degree of scatter, and the sample loop and column of the chromatograph frequently plugged although filters were used in the sample line. Apparently tar condensation occurred in the chromatograph even at 150°C in a dilute system. In addition, the very small system volume and short residence time meant that any fluctuations in feed rate or gas rate, or fluctuations due to momentary plugging, were not damped out, but were transmitted through the system. Such fluctuations would cause corresponding composition changes, and the instantaneous small samples for the chromatograph allowed the full range of these fluctuations to be observed in the results. In an attempt to improve on this scatter in results, a capacitance was added to the system (after Run 44) in the form of a two litre or four litre glass bulb maintained in an oil bath at 150°C. Gas samples for the chromatograph were then withdrawn from the bulb. While this device gave somewhat improved consistency for water analysis, it did not give the level of reproducibility desired. In succeeding runs a glass cyclone was added before the gas bulb to remove char which otherwise blew into the gas sample bulb and could plug the chromatograph sample loop. After Run 53, the use of the large gas sample bulb was discontinued, and hot gas samples for the chromatograph were withdrawn from the cyclone.

The total volume of gases collected during a run, a quantity required to determine gas yields, was measured prior to Run 68 by recording gas flow rates and the time of running. After Run 68, the CH_4 content of the gas collecting bag was measured, a known volume of 100% CH_4 injected into the bag, and the concentration measured again. From these two values the total gas volume was calculated. In nearly all cases, the two values, from flow rates or from the CH_4 concentration marker, agreed well, and as a result, both methods of determining volumes were used as appropriate.

After Run 68, a larger fluid bed reactor with a net volume 154.6 ml. was designed and used, primarily for caking coals. Because some agglomeration always occurred in the bed, and some caking on the walls with these coals, the larger reactor dimensions usually allowed a run to be completed before these phenomena prevented operation. The details of this larger reactor are shown in Figure 1. The injection tube in this reactor could be air- or water-cooled if necessary to prevent plugging when caking coals were fed. Interchanging the large and small reactors allowed a wider range of residence times to be used also. Within the experimental accuracy, the yields obtained in the two reactors were the same at the same reaction conditions (see results of residence time variation for lignite given in Table 30).

The analysis of volatile organic products presents a problem. If these compounds are condensed, then they will be lost in the subsequent solvent washing and evaporation steps. An attempt was made in most of the runs to measure BTX (benzene, toluene, xylene) fraction and C_6 - C_8 hydrocarbons directly in the hot gas sample. However, apart from the problems mentioned earlier of fluctuating sample composition, and sample loop plugging, the thermal conductivity detector of the on-line Carle gas chromatograph was not sensitive to these compounds in the low concentrations existing in the product gas stream. By the conclusion of this program, it was assumed on the basis of vapour pressure calculations that most of these volatiles would not reach saturation pressure and therefore were contained entirely in the gas collected. Where BTX or C_6 - C_8 are not reported separately in later runs, they are included in the yield of the C_4 fraction, which was calculated from the areas of the chromatographic peaks of higher molecular weight compounds than C_3 obtained in the GC analysis of the product gas employing an FID detector for high sensitivity. However, minor yields of compounds of intermediate volatility may still be unaccounted for.

When high tar yields were obtained, for example, from Devco high volatile bituminous coal, a heavy coal tar fog formed in the condensers, and this fog carried through to the final clean-up filters which quickly became plugged. In an effort to solve this problem, two designs of liquid scrubber were used in place of the glass condensers, with solvent used as the scrubbing liquid. However, neither packed columns nor co-current flow air-lift type scrubbers were very effective in removing the tar aerosol, and the product gas became loaded with solvent

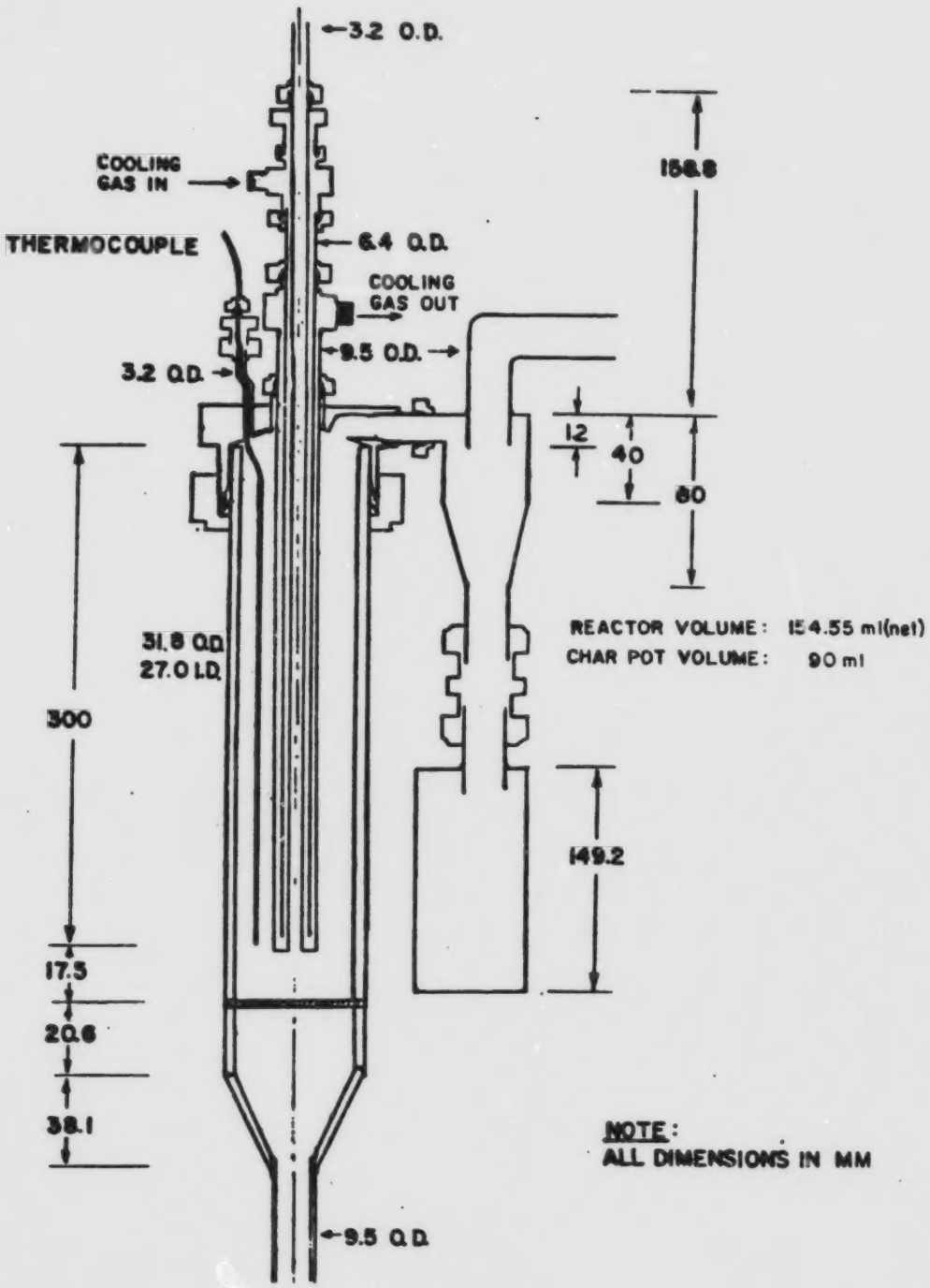

Figure 1 Details of Large Fluid Bed Reactor.

fumes. If a chlorinated solvent was used, these fumes were very deleterious to the chromatographic equipment. Therefore, the use of liquid scrubbers was discontinued and parallel, oversized filters were used instead to give sufficient filtering capacity to allow a run to be completed.

By the conclusion of the present program, a Karl Fischer water titration apparatus was available, and water yield was then determined by analyzing the liquid condensate and all solvent washings for H_2O before evaporation, and correcting for a blank solvent determination. To this was added the water content of the product gases to arrive at the final total water yield. This method yielded more consistent, and higher, values for water in the products than other approaches.

In most of the results given here, tar was removed from the apparatus by washing with methylene chloride and then with acetone. In later runs, a single mixed solvent of acetone/methylene chloride was used, and subsequently, a mixed solvent of methanol/methylene chloride, inasmuch as the latter gives less interference in the Karl Fischer titration.

RESULTS AND DISCUSSION

Results are presented in terms of the objectives described earlier. Cross comparison of these results has been done where desirable, so that data from a given run may be presented in more than one section.

Materials Used

In the results reported in this work, a total of eight coals were used as listed below. All samples were obtained from the Energy Research Laboratories of CANMET, Bells Corners, Ontario.

1. Forestburg - a high volatile Alberta sub-bituminous coal.
2. Highvale (Wabamun) - a medium volatile Alberta sub-bituminous coal.
3. Devco - a high volatile bituminous Nova Scotia caking coal.
4. Balmer - a low volatile bituminous British Columbia caking coal.
5. McIntyre - a low volatile bituminous Alberta caking coal.
6. Lignite (Saskatchewan Estevan) - a strip mined Saskatchewan lignite. Two samples of different characteristics were used (Lignite 1 and 3).
7. Hat Creek - a high ash, low volatile British Columbia sub-bituminous coal.
8. Sukunka - a medium volatile British Columbia bituminous caking coal.

In summary, one lignite, three sub-bituminous, and four bituminous caking coals were used. All but one of these coals was from Western Canada.

Proximate analyses of the coals are given in Table 1. Ultimate analysis values are given in Table 2. The elemental and proximate analyses were done by various sources, as noted. It was observed that both proximate and ultimate analyses for the same coal from different sources often varied widely, but many of the discrepancies disappeared if the analyses were compared on a moisture- and ash-free basis.

Table 1

Proximate Analyses

Type	Ash %	Moisture %	FC %	VM %	FC maf %	VM maf %	Oil Yield Fischer maf (3) %	FSI %
Estevan Lignite I {2}	8.25	28.4	34.75	28.61	54.85	45.15	-	0
Estevan Lignite 3 {1}	6.29	7.93	42.67	43.11	49.74	50.26	-	
Forestburg {1}	6.5	10.0	41.96	41.31	50.25	49.47	-	0
Highvale {1}	10.7	17.3	44.50	29.17	61.80	40.51	5.9	0
Hat Creek {1}	50.7	4.0	14.8	30.5	32.67	67.33	-	0
MacIntyre {2}	7.47	0.79	74.24	17.50	80.92	19.08	3.7	4.5
Balmer {2}	9.78	0.64	69.71	19.87	77.82	22.18	6.4	4.0
Sukunka {1}	9.00	1.88	69.9	21.1	78.4	23.7	5.2	3.7
Devco {1}	2.9	1.2	60.96	34.98	63.56	36.47	14.2	8.5

{1} Analysis by Coal Research Laboratory, University of Waterloo.

{2} Analysis by Energy Research Laboratories, CANMET.

{3} Furimsky et al (1981)

Table 2

Ultimate Analyses

maf basis

Type	C %	H%	S%	N%	O % (by difference)	H/C
Sask. Lignite I (2)	70.82	4.75	0.64	1.28	22.51	.80
Sask. Lignite 3 (1)	71.2	4.24	N.D.	1.64	22.9	.71
Forestburg (1)	71.2	4.50	0.60	1.53	22.2	.76
Highvale (1)	75.4	4.1	0.2	1.10	19.3	.65
Hat Creek (1)	60.36	2.8	N.D.	1.54	32.7	.56
MacIntyre (2)	93.13	4.66	0.46	1.30	0.46	.60
(1)	88.68	4.4	N.D.	1.2	5.7	.60
Balmer (2)	90.36	4.79	0.30	1.26	3.29	.64
(1)	89.08	4.28	N.D.	1.45	5.19	.58
Sukunka (2)	86.2	4.53	0.69	1.75	3.1	.63
Devco (2)	87.14	5.50	1.09	1.73	4.54	.76
(1)	86.33	5.48	N.D.	1.82	5.28	.76

(1) Analyses by Coal Research Laboratory, University of Waterloo.
(2) Analyses by Energy Research Laboratories, CANMET.

The coals used showed a wide variation in volatile matter. As pointed out by Furimsky (1981) however, a high volatile matter value does not correlate with high liquid hydrocarbon yield for lignites or high volatile sub-bituminous coals from Western Canada at least, not on the basis of the Fischer or Gray-King assay. All the coals used were relatively low in sulfur. A very large difference in oxygen content is apparent between the lower rank lignite and sub-bituminous coals and the higher rank bituminous coals. All the coals used except for the Devco Eastern Canadian coal had a substantial ash content. Since ash content is thought to have some effect on promoting gasification reactions, this factor may be classed as a less desirable feature if maximum production of liquids is a goal.

All coals were ground and screened to -149 +74 μm (-100 +200 mesh) and this was used as the standard feed size unless otherwise noted, e.g. in tests to determine the effect of particle size. Most of the coals were used as received except for the lignite which had to be air-dried to about 7.0% moisture before it could be fed at a constant rate from the low rate feeder.

Effect of Temperature

In the results given in the following sections, the definitions of "tar" and "gas" are usually consistent. In most cases, the "gas" yield quoted includes hydrocarbons to at least C_4. The "tar" yield is normally the residue left from solvent evaporation after filtering, and the BTX (benzene-toluene-xylene) fraction and the C_4 - C_8 fraction are often reported separately. If the data is available, these fractions have been added to the tar and reported as "liquid hydrocarbons" or in plots, the total is shown as "tar" if fractions are not separately identified. In general, the "tar" amount reported includes volatile hydrocarbons where these are not given separately.

1. Saskatchewan (Estevan) Lignite

Although two samples of Saskatchewan lignite (Lignite 1 and Lignite 3) were used, and a mixture, the majority of pyrolysis runs were carried out with Lignite 3, and therefore, the results reported are for this lignite. The two samples did not appear to differ except to a minor degree in ultimate composition, in any event, although differences in yields of various products that were significant could be detected. Therefore, detailed comparison is not made between the two lignite samples. Also, unless noted, all yields are expressed on a moisture and ash-free basis (maf).

The yield of tar and total volatiles is shown in Figure 2 and data is given in Table 3. Reactor Type 1 is the small reactor (net empty volume 23.3 ml) described in earlier reports, with an uncooled feed injection tube. Type 2 reactor is the same reactor but with a jacketed feed injection tube to allow air or water cooling of the feed, if desired. The "large" reactor is the unit shown in Figure 1 with a net empty volume of 154.6 ml.

A comparison of results for Lignite 1 and Lignite 3 at 500°C can be seen from the data for Runs 55 and 65 or Runs 56 and 66. Lignite 3 produced significantly less tar than Lignite 1, although gas and char yields were comparable. However, a very limited amount of Lignite 1 was available and only the first three runs shown in Table 3 were carried out with this sample. All other tests on lignite were done using Lignite 3.

Runs 61, 91 and 84 allow a comparison of the small and large reactors to be made. Although tar and yields are a little higher in the large reactor than in the small reactor, the values are within the range of experimental error for replicate runs. Gas and char yields indicate comparable performance in the various reactor types used. The comparison can also be seen in Figures 2 to 8 by comparing results at 650°C.

The tar yields given in Figure 2 for Lignite 3 show a maximum of about 10% maf at 650°-700°. Total volatiles are of the order expected for this lignite. Figure 3 shows the char yields for Lignite 3 also, and indicate a decrease in char obtained

Table 3

Product Yields
Saskatchewan Lignite -149 +74 μm
N_2 atm., 0.45 sec. residence time (except where noted)
maf weight %

T (°C)	Run	Gas	Tar	Char	BTX	H_2O	Total
500	55[1]	8.2	10.8	72.9	0.23	4.9	97.1
600	56[1]	10.4	10.4	69.0	0.23	6.5	95.8
700	57[1]	16.1	7.6	61.2	0.24		82.7
500	65[2]	9.5	6.5	72.6	0.18	11.9	100.7
550	63[2]	11.9	7.7	69.2	0.22	4.9	96.8
550	64[2]	10.7	6.9	72.1	0.33	10.8	100.8
600	66[2]	13.8	8.4	67.8	0.42	8.3	98.6
600	67[3]	12.6	8.9	69.6	0.32	5.4	96.9
650	61[2]	13.9	9.4	61.9	0.36	9.2	94.8
650	84[4]	14.6	10.3	63.7	0.50	4.6	93.5
650	91[2]	19.0	9.9	64.1	0.50	5.9	99.4
750	60[2]	23.5	6.8	59.3	0.57		90.2

Notes: [1] - Lignite 1, Reactor Type 2 (6.7% moisture, 10.5% ash)
[2] - Lignite 3, Reactor Type 1 (7.0% moisture, 9.1% ash)
[3] - Lignite 3, Reactor Type 2 (7.0% moisture, 9.1% ash)
[4] - Large Reactor.

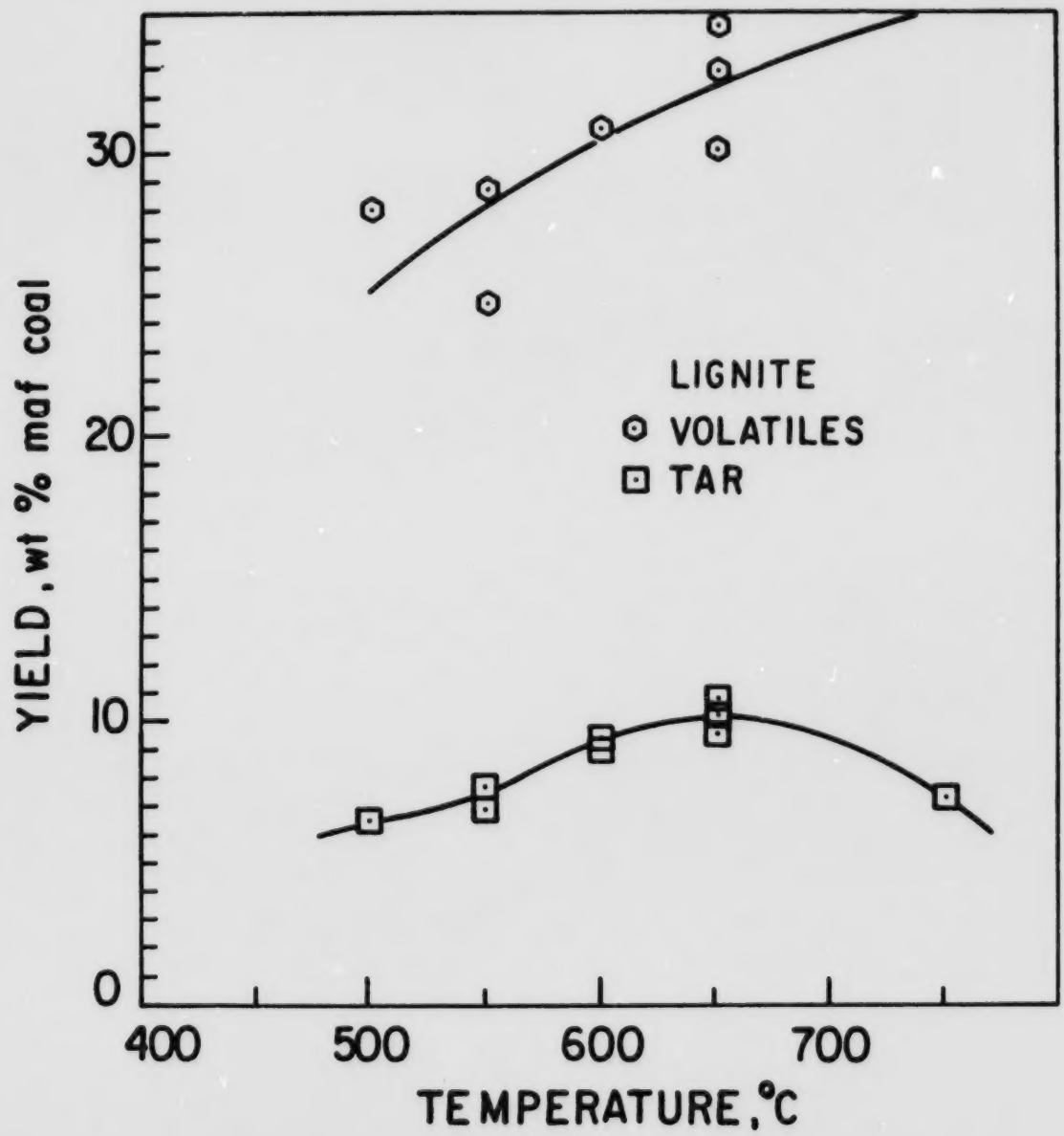

Figure 2 Tar and Volatiles Yield from Saskatchewan (Estevan) Lignite 3, -149 +74 μm, N_2, 0.45 S.

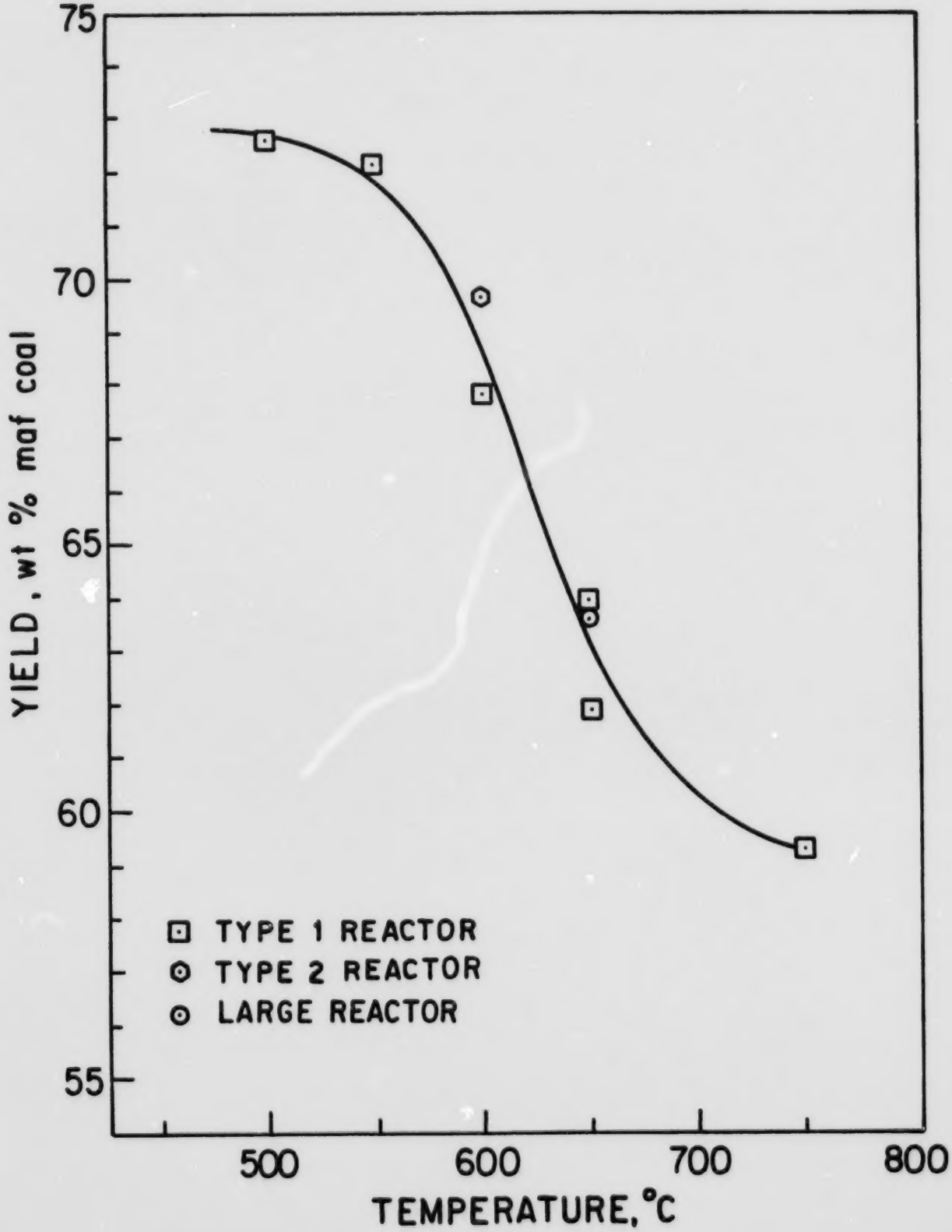

Figure 3 Char Yields, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

from 73% at 500° to 59% at 750°. This drop in char yield is accompanied by increases in gas yield and in tar yield. The char from lignite was very reactive, and care was required in handling to prevent spontaneous combustion when fresh char was exposed to air, even at room temperature.

The yields of various gases are shown in Figure 4, and the hydrocarbon gas yields in Figure 5. A feature of lignite is the large yield of CO_2 and at higher temperatures, of CO as well. From Table 3, it can be seen that a considerable amount of pyrolytic water is also formed. An estimate at 650° indicates that about 61% of the original oxygen incorporated in the lignite is rejected as CO_2, CO or H_2O on pyrolysis.

Figures 6 and 7 give the results of elemental analyses for tars and chars from Lignite 3. The carbon content of the tars increases slightly with temperature while the hydrogen content decreases steadily. As a consequence, the H/C molar ratio in the char decreases steadily with temperature, as shown in Figure 8. It would appear that better quality liquids are produced at lower temperatures, and hence some optimum condition involving quality vs yields might exist for the liquid product. However, these liquids still contain a fair amount of oxygen (10-15%), and may therefore also contain small amounts of dissolved water which would slightly overstate the hydrogen content associated with hydrocarbons. Water content was not determined on these tars. However, it is believed that the water content, if any, would be small after solvent evaporation, probably less than 5%. The trend shown in Figure 8 is therefore a valid one even though it may contain some error.

The char shows an even stronger change in the H/C ratio as the temperature of pyrolysis increases, decreasing from a value of 0.53 at 500° to 0.30 at 750°. The hydrogen which is lost from the char, as well as the much smaller amount from the tar, appears as light hydrocarbon gases (see Figure 5) or as BTX and C_4 - C_8 fractions.

Some comment on elemental analyses should be made. The micro analytical techniques currently in use for C/H/N/S determinations such as those done in our laboratory (Perkin-Elmer 240C Analyzer) are far from ideal for heterogeneous

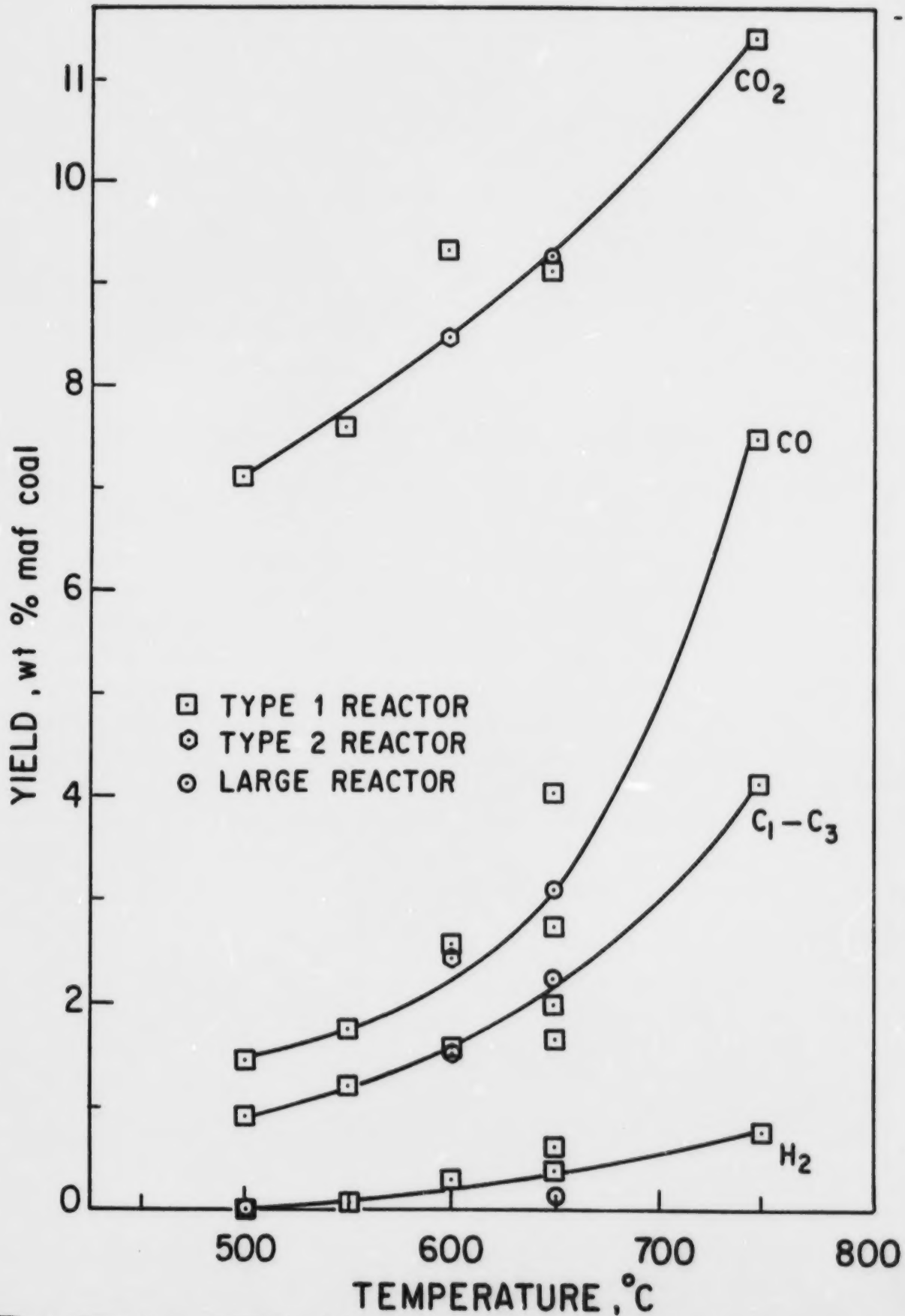

Figure 4 Gas Component Yields, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

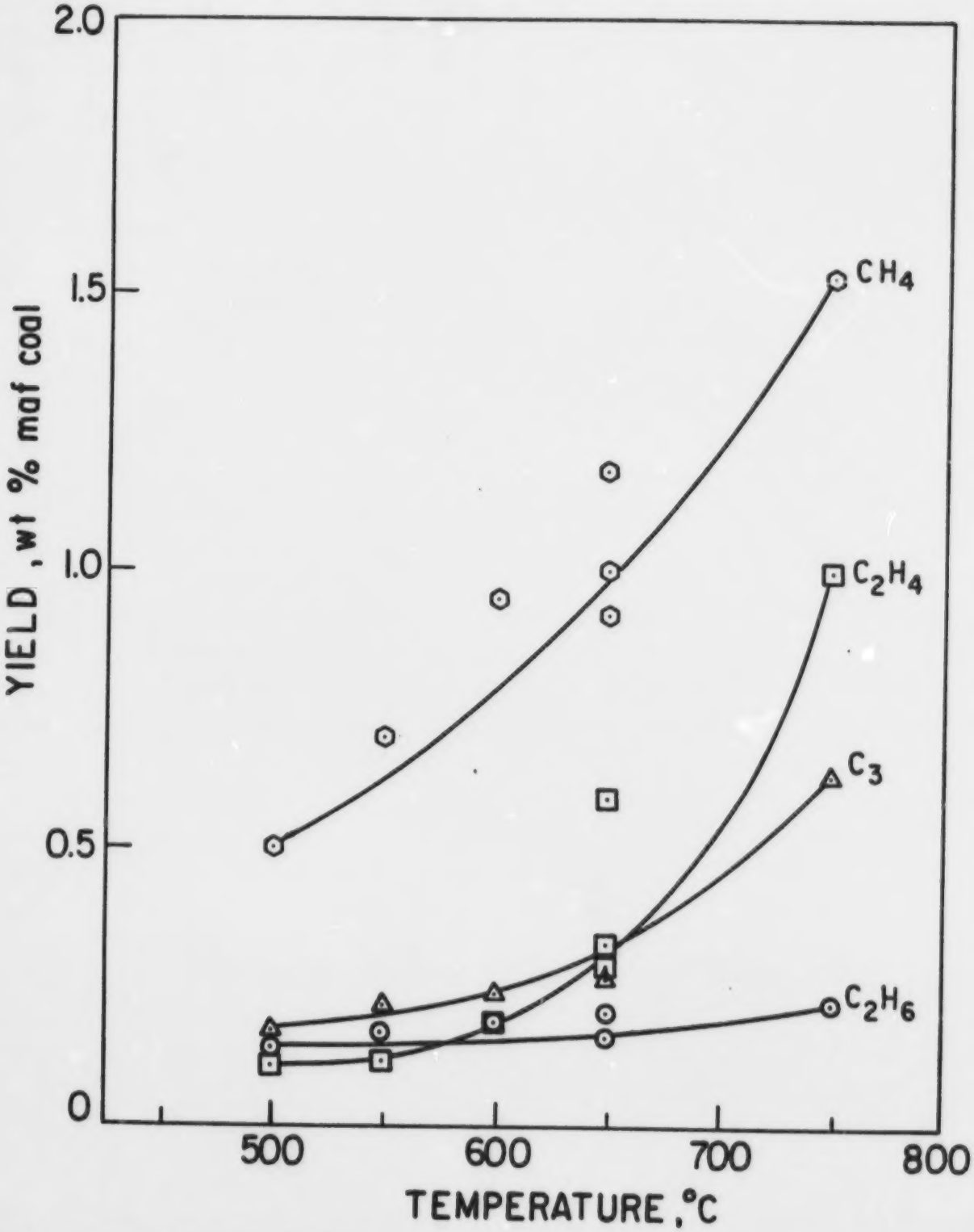

Figure 5 Hydrocarbon Gas Yields, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

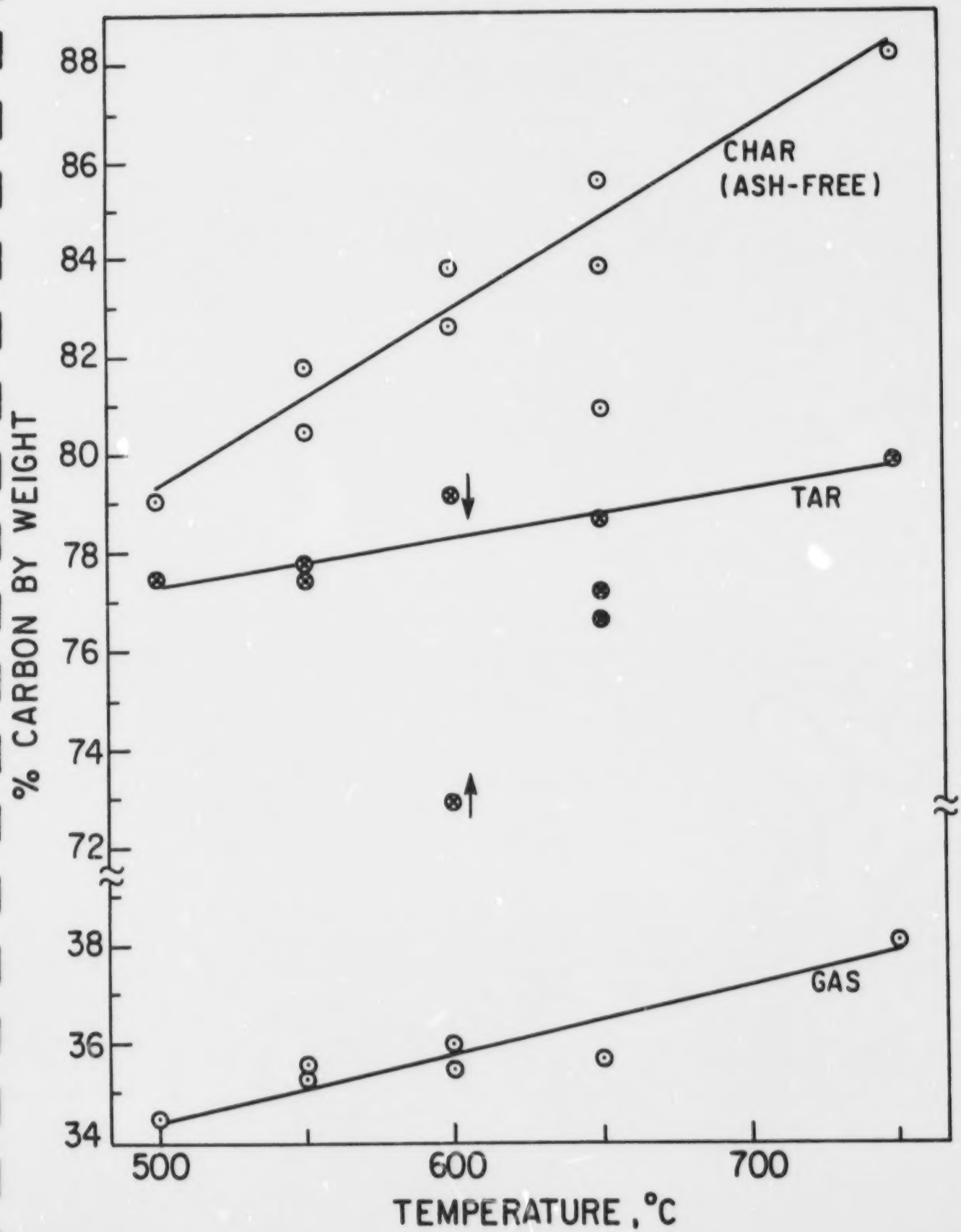

Figure 6 Carbon Analyses of Products, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

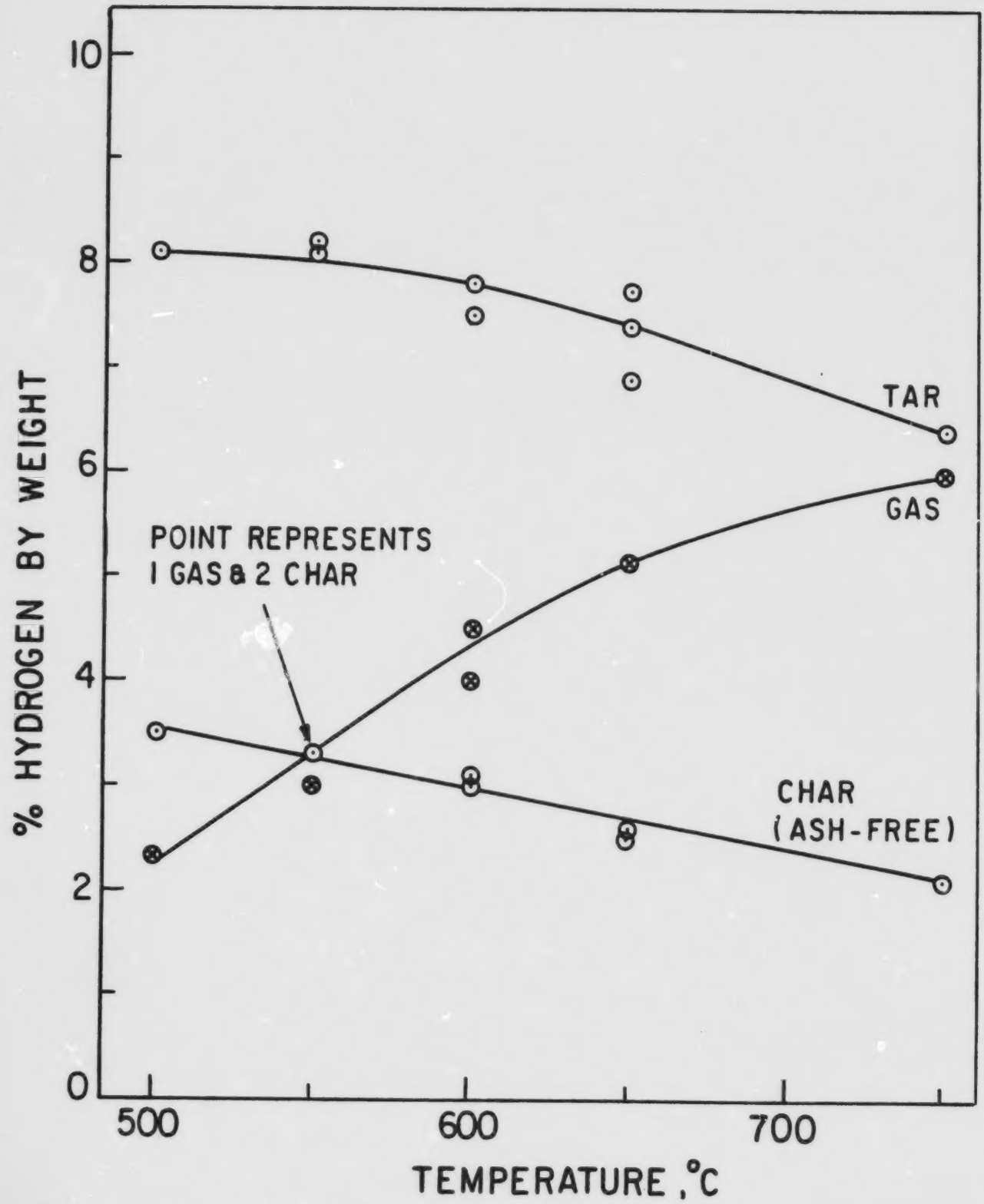

Figure 7 Hydrogen Analyses of Products, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

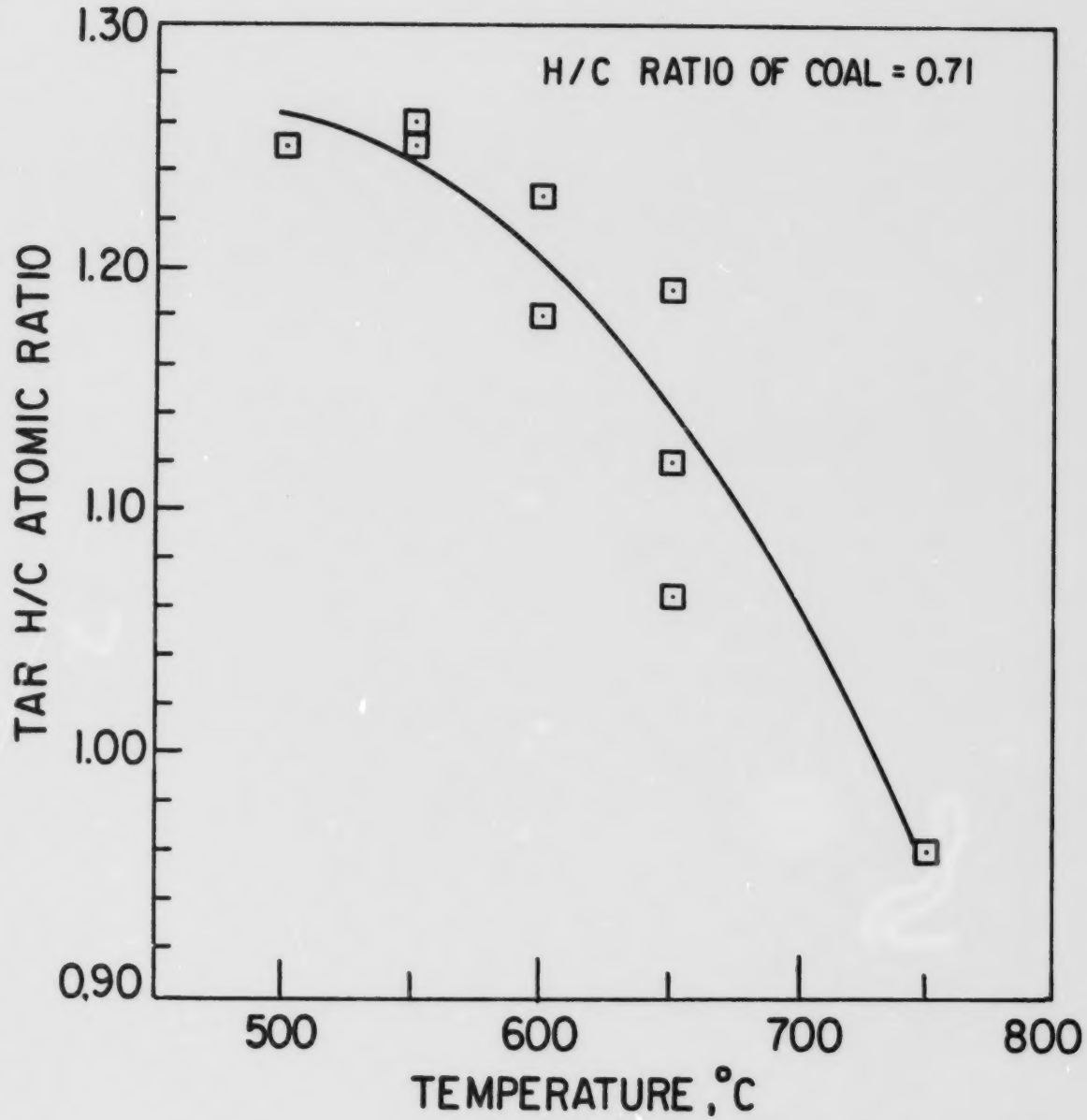

Figure 8 Atomic H/C Ratio of Tars as a Function of Temperature, Sask. Lignite 3, -149 +74 μm, N_2, 0.45 S.

materials like char and coal. The use of only a few milligrams of sample makes it extremely difficult to obtain representative samples. This can be partly offset by careful sampling techniques and by multiple determinations. However, these precautions negate most of the advantages of using micro analytical techniques. Our experience has been that results in a series of tests such as those done on the Lignite 3 char for example only show rational trends when compared on an ash-free basis with the ash being determined for each sample. Apparently, much of the coal ash is not homogeneously distributed, and the ash content of very small samples can therefore show wide variations.

In the present work, there have been continuing difficulties with analysis, particularly of solids, using the Perkin-Elmer 240C. Skilled operation is required, constant maintenance, and operating flexibility for different samples. By repeating analyses, sending samples to external laboratories as a check, and employing special operators, most of the elemental analysis results obtained in this work are fairly reliable. In some cases, especially for chars, difficulty has been experienced in getting acceptable C values. It is now felt, however, that the current operator and experience allow quite reliable results.

2. Forestburg Sub-Bituminous Coal

A number of pyrolysis tests on Forestburg coal had been carried out in an earlier program, so a limited number of additional tests were done. Results are given in Table 4 for temperatures from 500° - 700°, and the product yields are plotted in Figures 9 to 12. Typical results from earlier work are included together with the results from the current study. Good agreement was obtained with work done a year earlier by others in our laboratory using essentially the same apparatus, as shown by the comparison of gas, tar and char yields in Figures 9 and 10, indicating a satisfactory degree of reproducibility in the pyrolysis tests. Good reproducibility is also indicated by the fact that tests were never done sequentially as a variable was changed, but were done in random order.

Table 4

Product Yields

Forestburg Sub-Bituminous (maf)

-149 +74 μm, N_2 atmosphere, no catalyst, 0.44 secs., 9.85% moisture, 7.48% ash

Run	Temp °C	Char	Gas	Tar	BTX	H_2O	Total
52	500	76.23	11.54	6.05	0.30	2.84	96.96
48	550	69.35	14.66	7.68	0.29	5.23	97.21
45	600	63.77	16.86	8.71	0.31	-	-
46	650	58.52	17.87	9.68	0.37	-	-
49	700	56.10	21.64	8.64	0.42	9.00	95.80

Table 5

Gas Yields
(maf)

Forestburg Sub-Bituminous, 9.85% moisture, 7.48% Ash
-149 +74 μm, N_2 atmosphere, 0.44 sec.

Run	Temp °C	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3
52	500	0.02	2.99	7.57	0.52	0.11	0.16	0.17
48	550	0.11	3.70	9.23	1.00	0.16	0.21	0.25
45	600	0.08	4.23	10.55	1.10	0.18	0.30	0.41
46	650	0.33	5.08	10.25	1.33	0.30	0.21	0.36
49	700	0.46	6.25	12.08	1.46	0.52	0.25	0.46

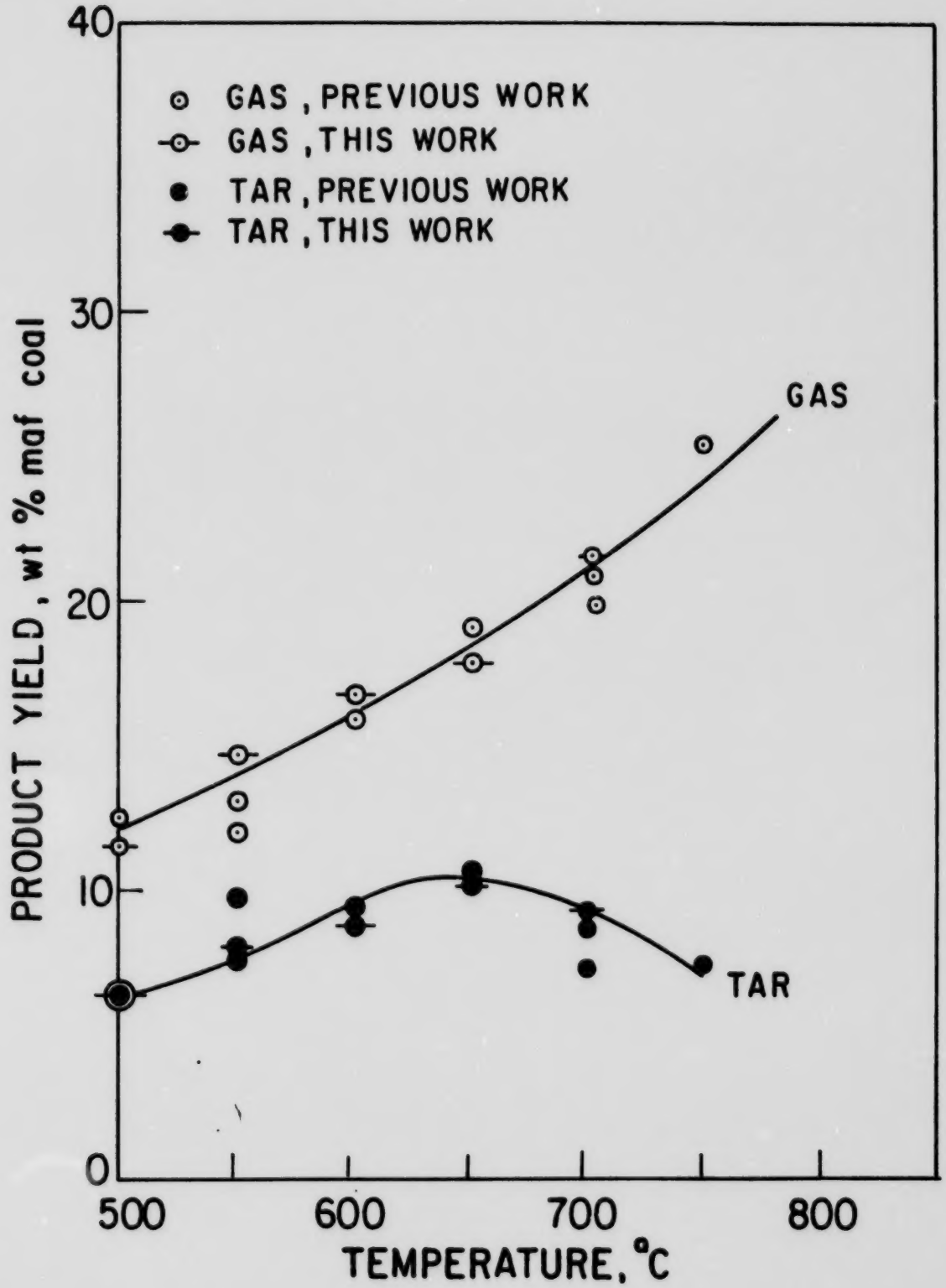

Figure 9 Gas and Tar Yields, Forestburg Sub-Bituminous, -149 +74 μm, N_2, 0.44 s

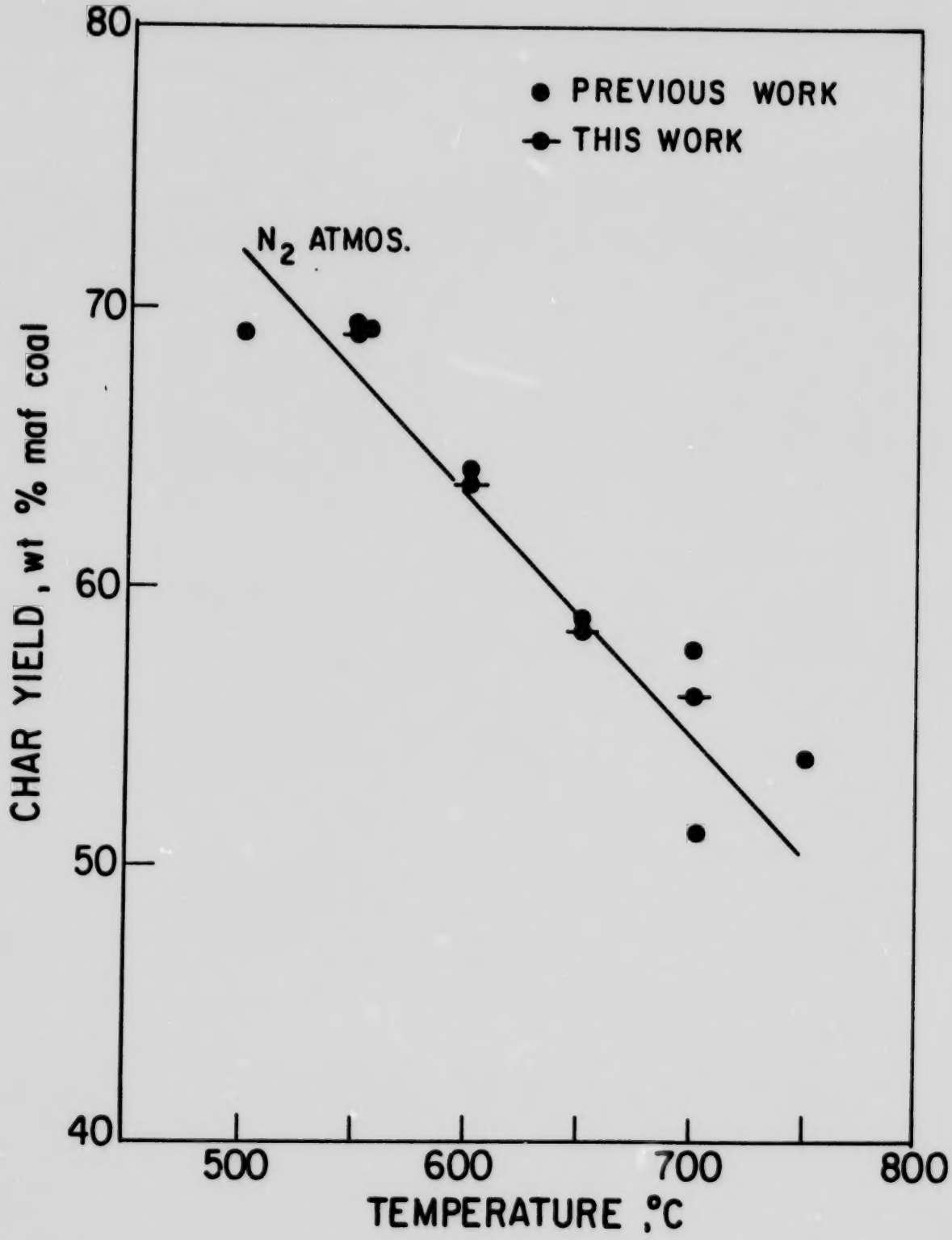

Figure 10 Char Yield, Forestburg Sub-Bituminous, -149 +74 μm, N_2, 0.44 S.

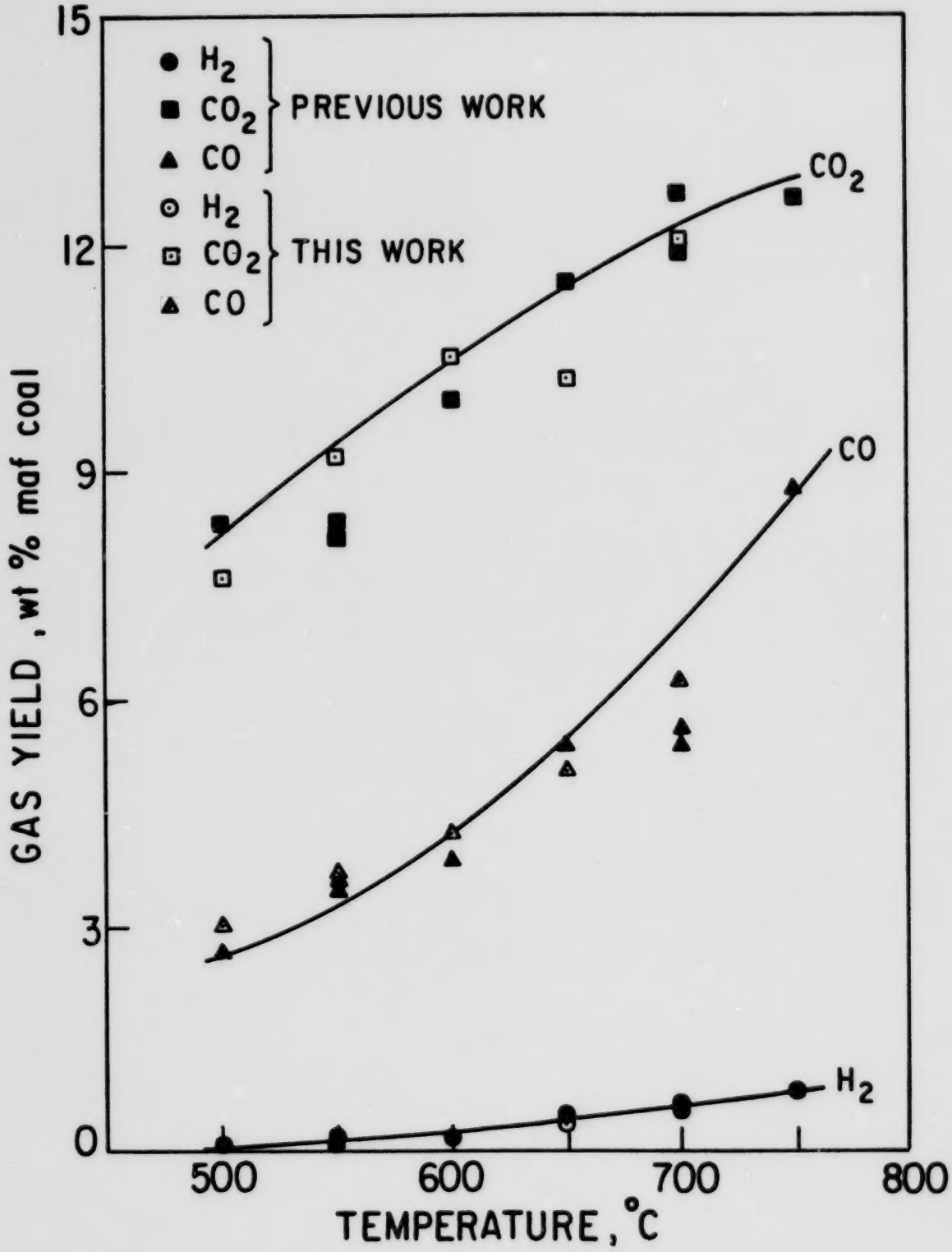

Figure 11 Gas Component Yields, Forestburg Sub-Bituminous, -149 +74 μm, N_2, 0.44 S.

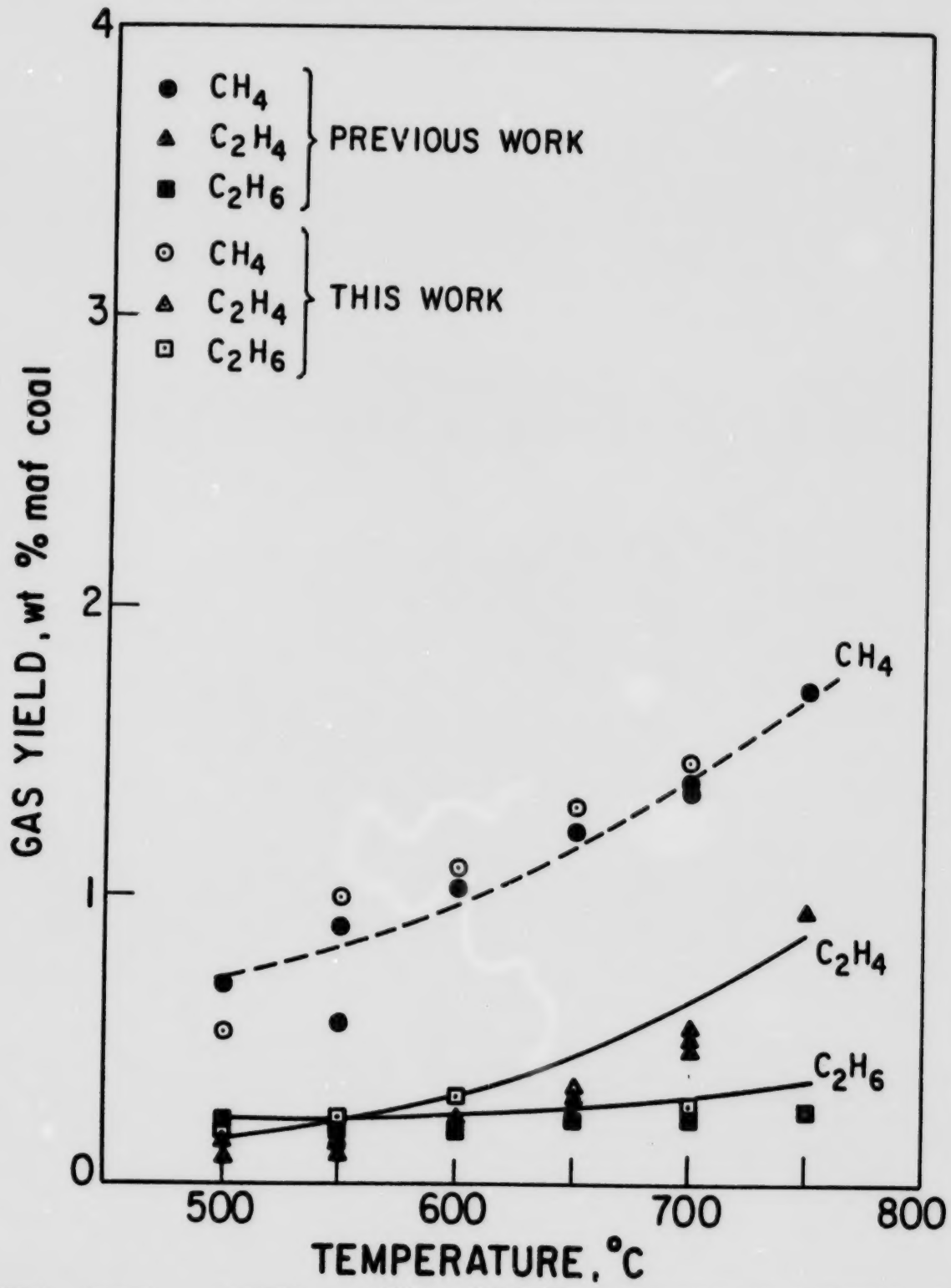

Figure 12 Hydrocarbon Gas Yields, Forestburg Sub-Bituminous, -149 +74 μm, N_2, 0.44 S.

Tar yields of about 10.5% were obtained; very much the same as those from Lignite 3. Forestburg and the lignite coal have very similar elemental compositions, and very similar proximate analyses on an maf basis, although one is classed as a lower rank than the other. Indeed, there is a great similarity also in yields of other products from the two coals, with the Forestburg coal giving slightly higher tar and gas yields and slightly lower char yields, but with very similar trends. Again, high CO_2 and CO yields are obtained, and at the optimum temperature for liquid production of 650°, some 80% of the oxygen in the coal has been rejected as CO_2, CO and H_2O. At higher temperatures, most of the oxygen in the coal is removed in this way.

Some elemental analyses of products is given in Table 6. As in the case of the Lignite 3 coal, the H/C ratio of both the tar and the char decrease with temperature, with the lost hydrogen appearing as light hydrocarbon gases.

3. Highvale (Wabamun) Sub-Bituminous Coal

Again, because a number of pyrolysis tests for this coal had been reported in earlier work, a limited number of tests were carried out. Results are given in Tables 7 and 8, and are shown plotted in Figures 13 to 16, together with some data from tests reported earlier (Scott et al, 1982). Results from the two sets of runs, performed some months apart by three different operators, show an acceptable degree of agreement.

Although the Highvale and Forestburg coal are quite similar in elemental composition, and both are classed as sub-bituminous coals, the Forestburg coal gives a significantly higher volatile matter yield than does the Highvale coal in a proximate analysis. Despite this fact, the Highvale coal gives a higher tar and BTX yield than does the Forestburg - about 11% liquid hydrocarbon vs 10%. Gas yield is lower and char yield significantly higher from the Highvale coal, although trends are very similar. As might be expected, the yields of all gas products are lower from the Highvale coal, but only slightly lower for all gases except CO_2, which is significantly lower. Apparently, the Forestburg coal contains more carboxylic acid groups, and therefore yields more CO_2. This result also suggests that acid washing might be of more benefit for the Forestburg coal.

Table 6

Effect of Temperature on Product Analysis

Forestburg Coal, 9.85% Moisture, 7.5% Ash, N_2, 0.44 s.

Run	Temp °C		Analysis, weight % maf				
			C	H	N	O	H/C
52	500	Tar	77.4	8.5	0.8	13.3	1.32
		Char	75.3	3.7	1.6	19.4	0.59
40	650	Tar	74.54	6.83	1.9	16.7	1.10
		Char	89.79	3.29	2.5	4.4	0.44
41	750	Tar	74.15	5.58	2.3	18.0	0.90
		Char	86.97	2.73	1.7	8.6	0.38

Table 7

Product Yields

Highvale Sub-Bituminous
(maf Basis)

-149 +74 μm, N_2 atmosphere, no catalyst, 0.44 secs., 17.3% moisture, 10.7% Ash

Run	Temp °C	Char	Gas	Tar	BTX	H_2O	Total
85	500	78.46	9.19	5.07	0.21	1.9	94.82
51	550	78.20	10.70	7.17	0.18	-	
44	600	74.90	13.53	11.81	0.40	-	
47	650	69.10	15.85	9.99	0.43	4.17	99.54
50	700	69.72	18.06	10.25	0.50	-	

Table 8

Gas Yields
(maf Basis)
Highvale Sub-Bituminous
-149 +74 μm, 17.3% moisture, 10.7% Ash, N_2, 0.44 s.

Run	Temp °C	H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3
85	500	0.04	1.84	6.48	0.46	0.11	0.14	0.18
51	550	0.05	2.40	7.24	0.68	0.14	0.18	0.17
44	600	0.28	3.40	8.08	0.83	0.28	0.35	0.40
47	650	0.28	3.92	9.75	1.10	0.26	0.19	0.35
50	700	0.49	5.08	10.1	1.29	0.47	0.22	0.39

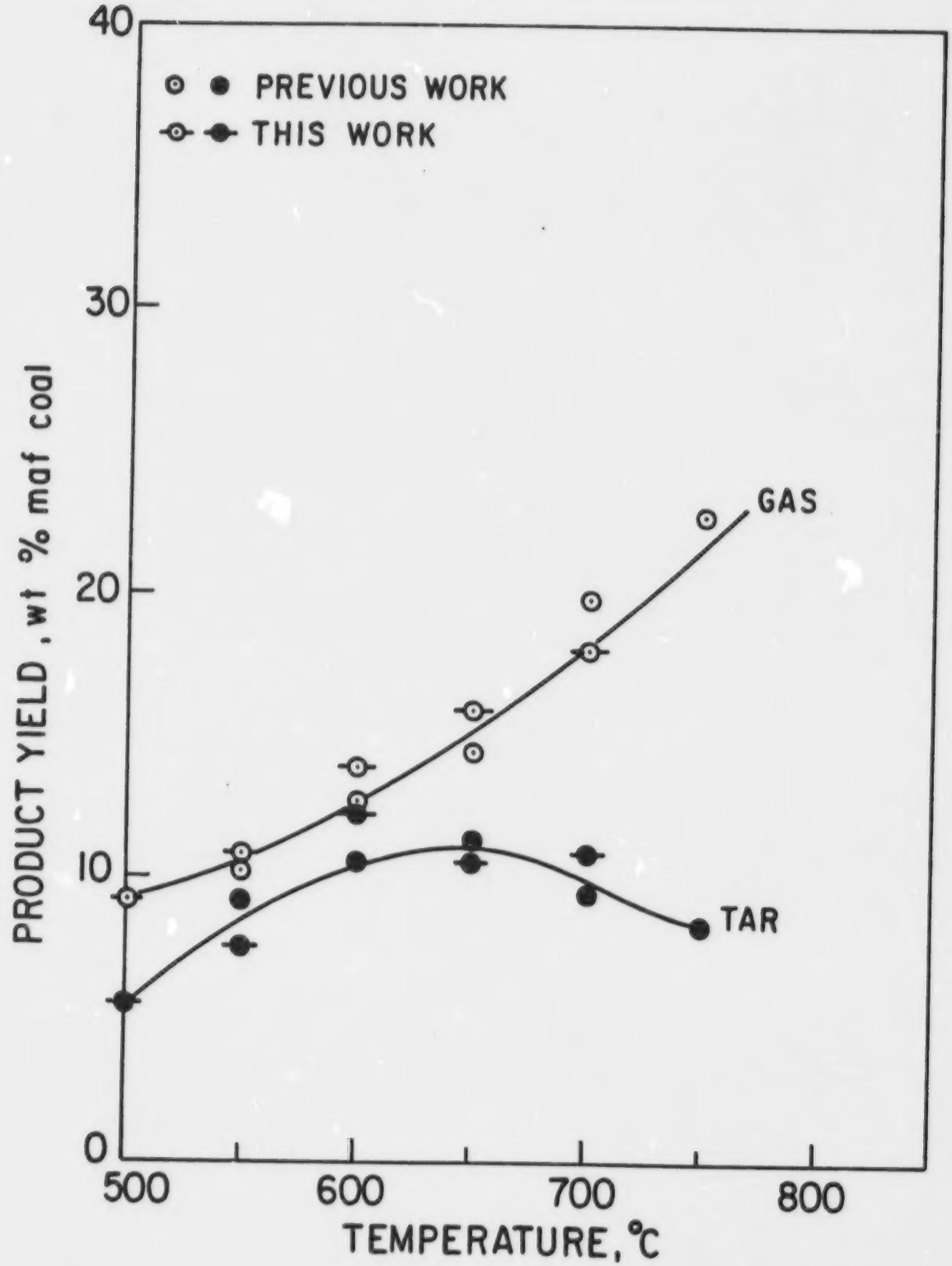

Figure 13 Gas and Tar Yields, Highvale Sub-Bituminous, -149 +74 μm, N_2, 0.44 S.

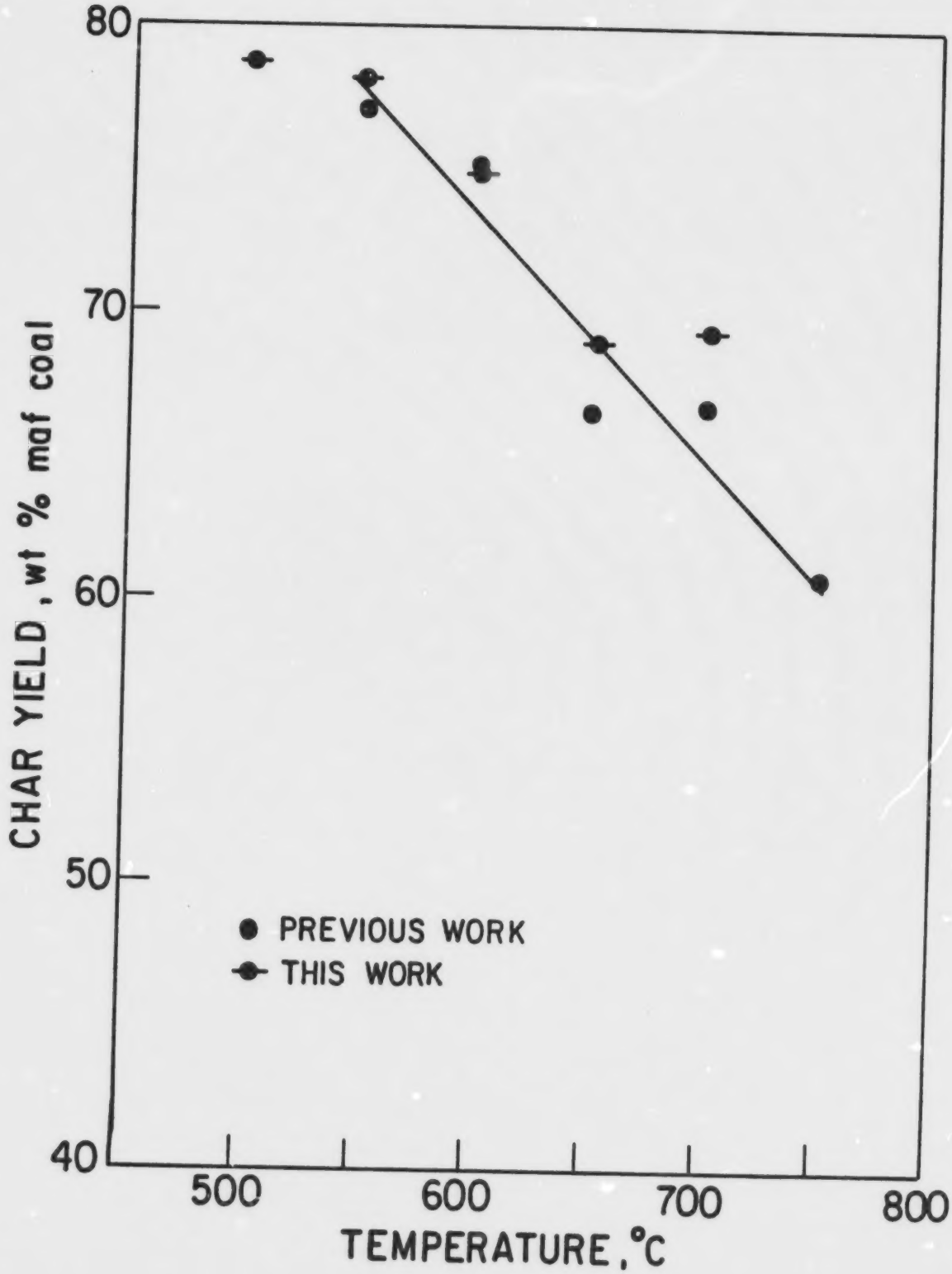

Figure 14 Char Yields, Highvale Sub-Bituminous, -149 +74 μm, N_2, 0.44 S.

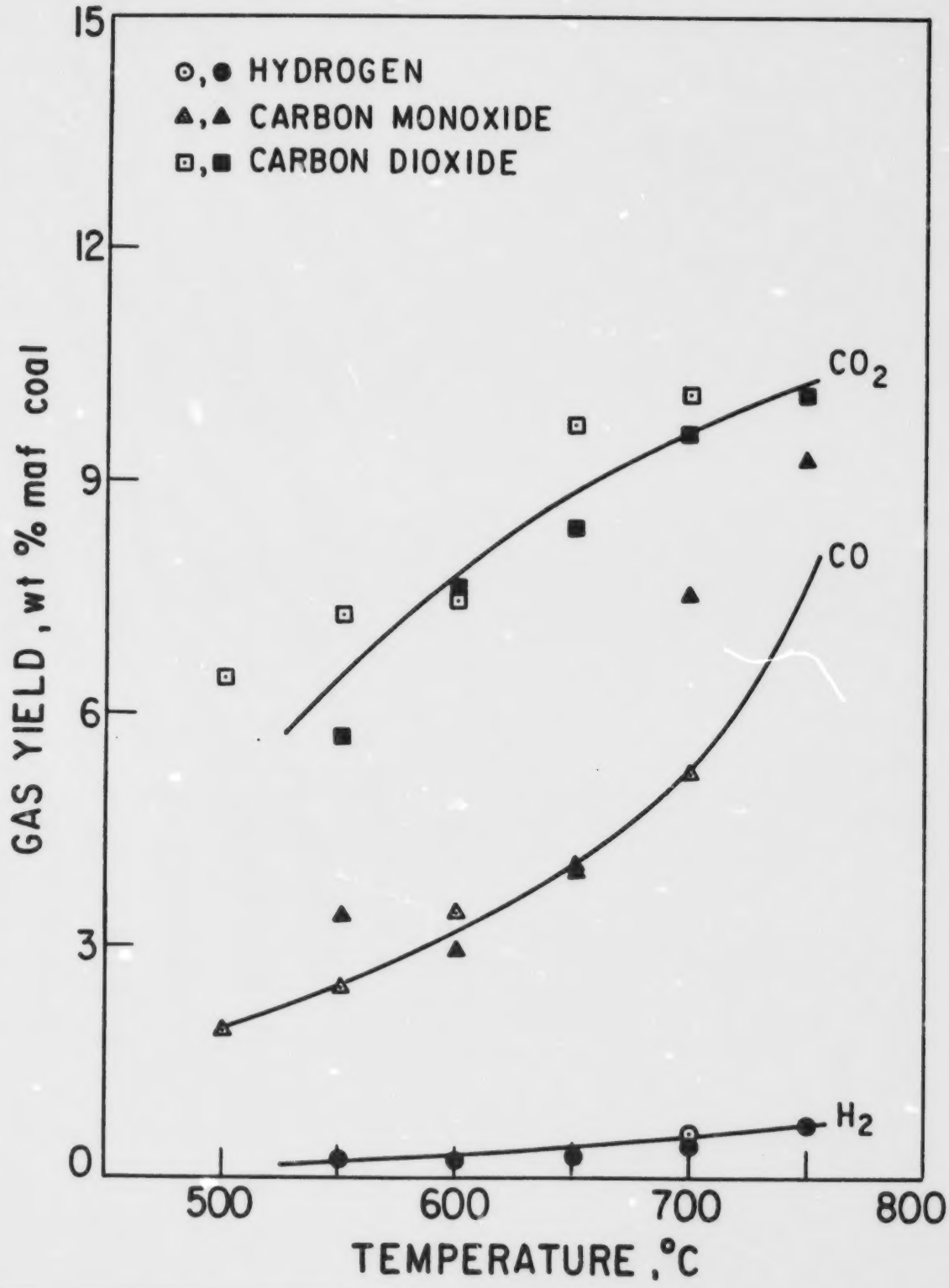

Figure 15 Gas Component Yields, Highvale Sub-Bituminous, 149 +74 μm, N_2, 0.44 S. Open symbols, this work; closed symbols, previous work.

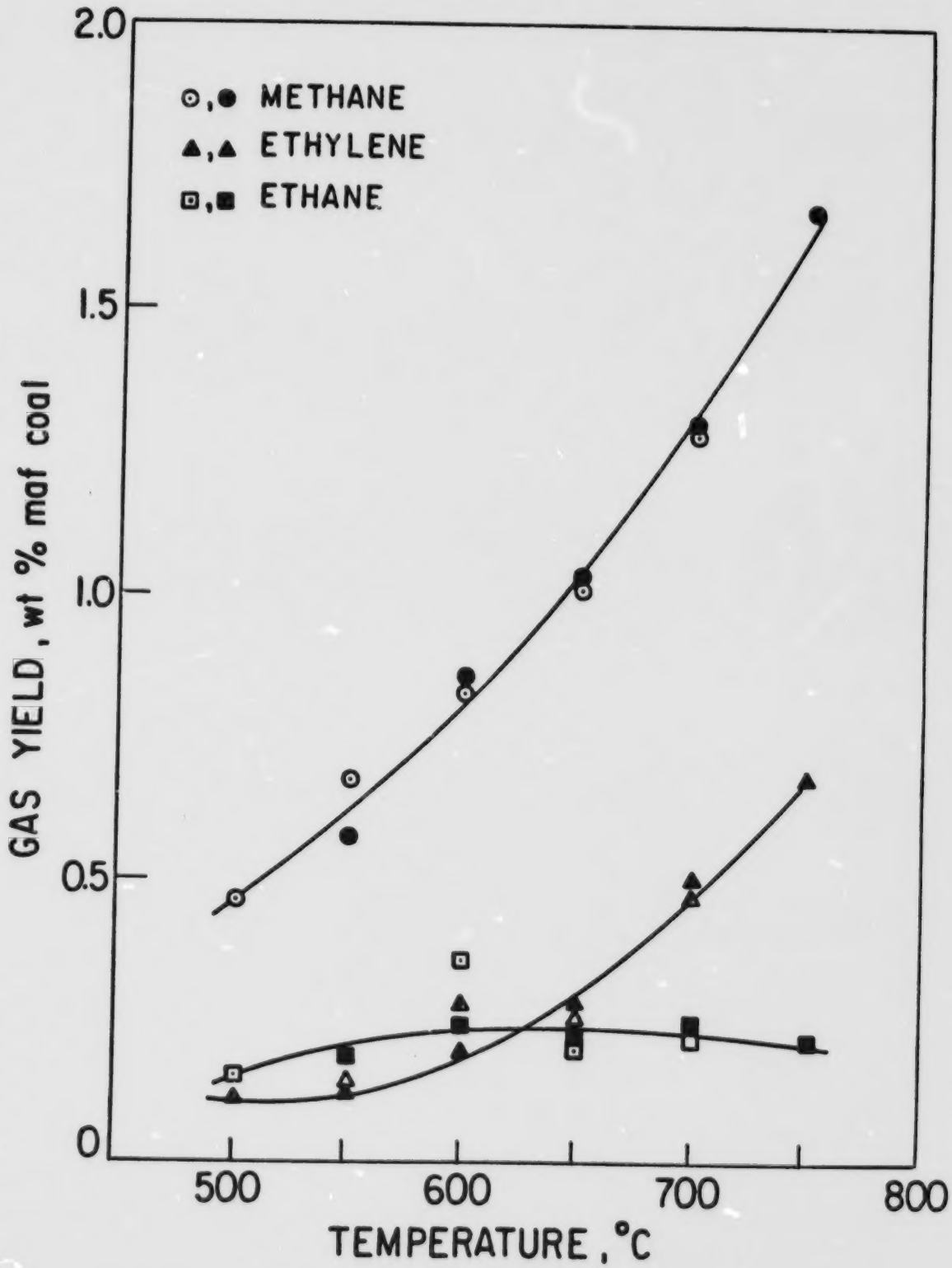

Figure 16 Hydrocarbon Gas Yields, Highvale Sub-Bituminous, -149 +74 μm, N_2, 0.44 S. Open symbols, this work; closed symbols, previous work.

Because of difficulties with elemental analysis procedures and results (from both in-house and external laboratories) at the time these tests were carried out, no reliable elemental analyses of products were obtained. Those that are available are given in Table 9. Anomalous values for both C (char of Run 43) and H (tar of Run 85) are apparent. Based on Runs 42 and 43, the H/C ratio of the tars appears to be about the same as that for tars from the Forestburg coal at the same temperatures. The same is also true of the H/C ratios of the chars. Again, these ratios show a significant decrease with temperature for both tars and chars.

An interesting comparison of tar yields is available because of work done at the Alberta Research Council on this coal, and additional results of others reported by them (Du Plessis, 1982). This comparison is shown in summary form in Table 10. The tar and light oil yield from any of the fast pyrolysis methods exceeds the yield in the Fischer or Gray-King assays by up to about 100%. This large yield of liquids over that predicted in the standard assay is common for many lower rank coals in particular. It is not a universal characteristic, however, and because of this it is difficult to use the Fischer assay as a means of predicting the yield of pyrolytic liquid hydrocarbons.

4. Hat Creek Sub-Bituminous Coal

Hat Creek coal was a very high ash (46-48%), high moisture content coal with a low volatiles content. The results of pyrolysis tests over the range of 500° - 700° are shown in Table 11 on an maf basis. The maximum yield of liquid hydrocarbons was obtained at 650° as for other low rank coals, but it amounted to only 5.5% maf (about 2.1% of the coal as fed). Gas yields were relatively high, significantly higher than the Lignite 3, Forestburg or Highvale coals, with very large amounts of CO_2 being generated, with yields of other gases being more comparable to those from other low rank coals. It would appear that the Hat Creek coal is in some respects more similar to a lignite, although the Hat Creek coal has a much higher oxygen content (32% vs 22%) and gives a much lower char yield (ash free) than does the Saskatchewan lignite. Apparently, much of the oxygen is present as carboxylic acid groups which can be readily split off, but which do not yield any significant liquids. Water yield is also high from this coal, but it could not be quantitatively measured in these runs.

Table 9

Effect of Temperature on Product Analysis

Highvale Coal, 17.3% Moisture, 10.7% Ash, N_2, 0.44 s.

Run	Temp °C		Analysis, weight % maf					
			C	H	N	O	Ash	H/C
85	500	Tar	69.31	3.33	N.D.			-
		Char	82.6	4.63	N.D.		9.85	0.67
42	650	Tar	77.2	6.84	1.40	14.6		1.06
		Char	77.9	2.73	1.73		10.0	0.42
43	750	Tar	77.7	5.6	2.5	14.2		0.86
		Char	68.3	1.94	1.28		6.7	0.34

Table 10

Pyrolysis of Wabamun (Highvale Coal)

Comparison of Yields by Various Methods

	Products (wt % maf coal)				
Method	Char	Tar & Light Oil	Water	Gas	Total
Fischer-Schrader[3] (550°C, 1.5 hr)	72.6	5.9	10.9	10.6	100
Fluid-Bed[4] (550°C, 0.44 sec)	78.2	7.3	-[5]	10.7	96.2[6]
Gray-King[3] (600°C, 1 hr)	69.5	6.6	7.9	16.0	100
Fluid-Bed[4] (600°C, 0.44 sec)	74.9	12.2	-[5]	13.5	100.5[7]
FTIR Vacuum[3] (650°C, 10 sec)	66.7	15.0[1]	11.4	6.9	100
Occidental Flash[3] (650°C, 2 sec)	64.0	14.2[2]	2.7	19.1	100
Fluid Bed[4] (650°C, 0.44 sec)	69.1 66.5	10.4 11.2	4.2 2.7	15.8 14.1	99.5[8] 94.4[9]
ASTM Proximate Analysis (950°C, 7 min)	60.4	39.6			100

1 Light oil estimate by difference.

2 Light oil is included partly in gas and partly in tar.

3 Reported in "Coal Conversion Research Program at the Alberta Research Council" by M.P. DuPlessis, Journal of Canadian Petroleum Technology, July-August, 1982, p. 79-88.

4 Experiments performed at UW.

5 Not reported.

6 Run 51

7 Run 44

8 Run 47

9 Run 22

Table 11

Pyrolysis of Hat Creek -149 +74 μm

15.4% moisture, 46.4% ash

0.45 sec. residence time, N_2 atm

Temp (°C)		500	550	600	650	700
Run #		129	130	128	127	126
Yield (maf wt%)	H_2	-	0.2	0.3	0.4	0.7
	CO	2.6	3.0	4.1	4.7	6.1
	CO_2	10.5	10.2	13.5	13.4	18.6
	CH_4	0.4	0.6	0.7	1.0	1.2
	C_2H_4	0.1	0.2	0.2	0.3	0.5
	C_2H_6	0.1	0.2	0.1	0.1	0.2
	C_3	0.2	0.2	0.2	0.3	0.4
	Gas	14.1	14.5	19.2	20.0	27.0
	Tar	2.6	3.1	3.0	4.5	3.2
	BTX	0.2	0.2	0.4	0.2	0.2
	$C_4 \rightarrow C_8$	1.0	0.7	0.8	0.8	0.9
	LHC[1]	3.8	4.0	4.2	5.5	4.3
	CHAR	56.9	56.3	51.8	49.2	39.7
	H_2O	-	-	-	-	-
Total		74.8	74.7	75.2	74.7	71.1

1 - LHC = light hydrocarbons = Tar + BTX + $C_4 \rightarrow C_8$

Table 12 gives the variation of elemental composition of chars and tars with temperature. The H/C ratio of the tar appears to show little change as pyrolysis temperature increases, but again it should be realized that this tar may contain some water in solution which would overstate the hydrogen content. The anomalously high result for the Run 128 tar may be due to this reason. On the other hand, the H/C ratio for the char, which is free of water, shows a steady decrease as temperature increases, with values very similar to those for other low rank coals. In spite of the uncertainty in tar hydrogen analyses, the typical H/C value of about 1.2 to 1.3 does not appear to be unreasonable.

The very low yield of liquids and the very high ash content indicate that the Hat Creek coal is probably not a suitable feed for a pyrolysis process. However, it may be possible that some pre-treatment, such as ash removal, or acid washing, would increase tar yields.

5. Balmer Bituminous Coal

The Balmer coal is classed as a low volatile bituminous caking coal with a low oxygen content and a high carbon content. Pyrolysis of Balmer bituminous coal was studied for temperatures from 500° to 700°C. A duplicate run was performed at 600°C as a reproducibility check. All runs were performed with a -100/+200 mesh coal feed under an N_2 atmosphere with a residence time of 0.8 seconds. This residence time was chosen even though it may not be optimal because it allowed the larger reactor to be used. Use of the large reactor is important for the bituminous coals because they have been found to agglomerate in the void space above the sand level in the reactor. Use of the large reactor allows more coal to be fed before reactor clogging is observed. A larger amount of coal feed is expected to give better closure for material balances. It is possible to achieve an 0.45 second residence time in the large reactor, but then run time becomes limited by the capacity of the gas collection system.

Product yields for these runs are presented in Table 13 and yields of major products are shown in Figure 17. The maximum tar yield occurred at 650°C and is quite clearly defined. A maximum in tar yield of 10.0 maf wt.% was found, with

Table 12

Effect of Temperature on Product Analysis

Hat Creek Coal, 15.4% Moisture, 46.4% Ash, N_2, 0.45 s.

Run	Temp °C		Analysis, weight % maf C	H	N	O	Ash*	H/C
129	500	Tar	77.37	8.13	0.0			1.26
		Char	68.49	4.13	1.26	26.1	51.60	0.72
130	550	Tar	73.41	7.91	0.20			1.29
		Char	75.18	3.60	1.72	19.5	43.63	0.57
128	600	Tar	75.86	10.49	0.06			1.66
		Char	80.42	3.67	0.67	15.2	49.04	0.55
127	650	Tar	72.67	7.37	0.90			1.22
		Char	83.29	2.91	1.55	12.2	61.05	0.42
126	700	Tar	78.38	6.87	0.49			1.05
		Char	79.30	2.58	1.51	17.6	56.27	0.39

* Determined as residue from C/H/N analysis. Theoretical value 68-75%.

Table 13

Product Yields
Balmer -149 +74 μm
N_2 atm., 0.8 sec. residence time 0.8% moisture, 8.8% ash

Temp. °C		500	550	600	600	650	700	500
Run #		95	97	96	98	93	94	58*
Yields (maf wt%)	Gas	1.2	1.6	2.4	2.1	3.9	3.3	1.0
	Tar	3.0	4.8	5.5	4.4	10.0	8.4	
	BTX	0.2	0.3	0.3	0.3	0.4	0.6	
	$C_4 \rightarrow C_8$	0.3	1.0	0.6	0.5	1.0	0.7	
	Tar + LHC	3.5	6.1	6.4	5.2	11.4	9.7	5.1
	Char	85.3	92.7	87.5	91.2	80.7	79.6	92.3
	H_2O	2.2	1.8	2.3	2.6	1.9	3.5	1.5
	Total	92.2	102.0	98.6	101.2	97.9	96.2	99.9

LHC = light hydrocarbon * 0.49 s Residence Time

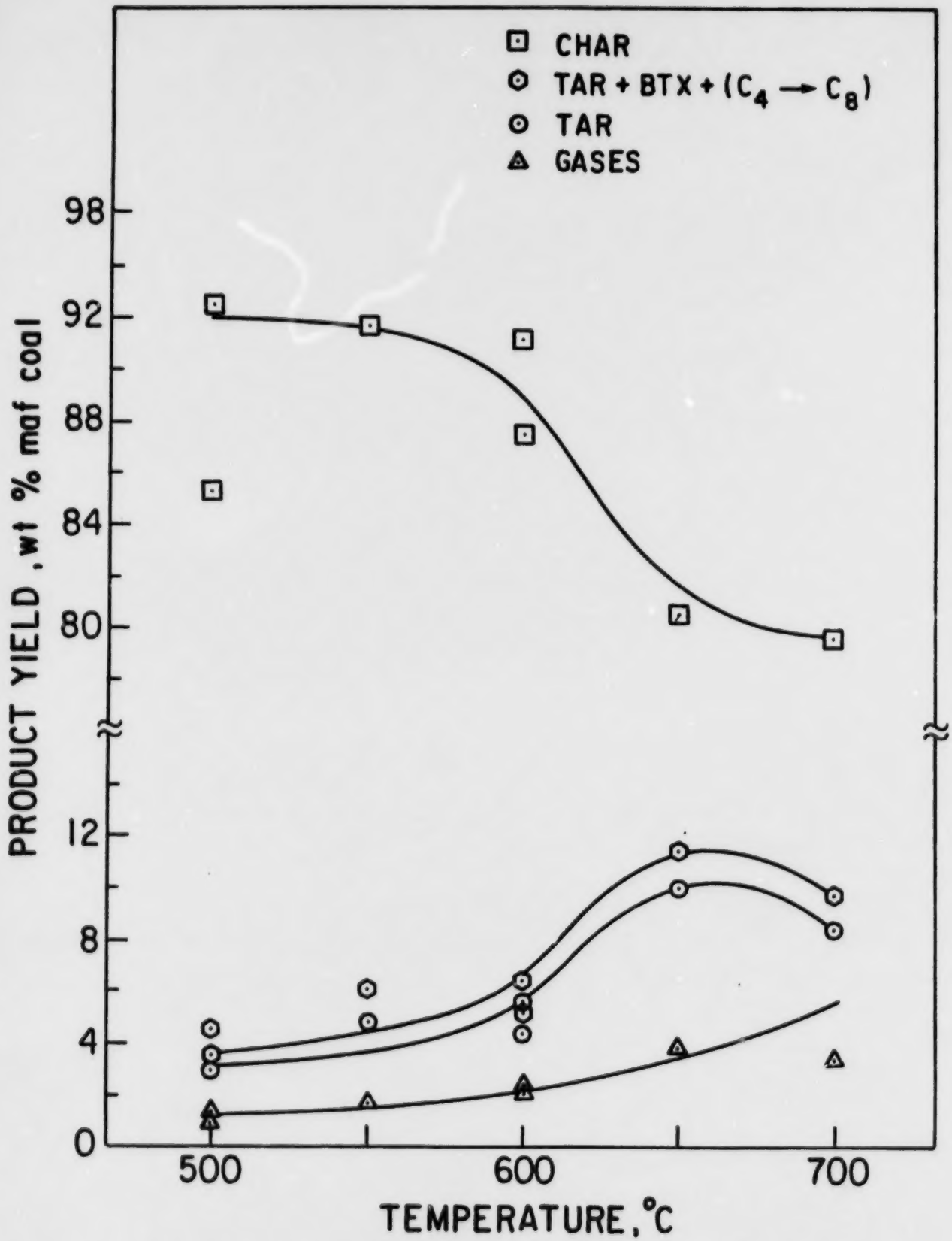

Figure 17 Char, Tar and Gas Yields, Balmer Bituminous, -149 +74 μm, N_2, 0.8 S.

BTX and light hydrocarbons accounting for an additional 1.4 maf wt.% of coal fed. The sharp increase in tar yield in the 600° to 650°C range is accompanied by a sharp decline in char yield.

The total gas volume for run 94 (700°C) had to be calculated using the rotameter settings rather than the CH_4 injection method used for the other runs due to a collection error. This could explain why the gas yield for this is lower than anticipated. A quantity of "Silver Goop" thread lubricant added to the reactor for run 95 (500°C) may have interfered with reactor weighing and caused the apparently low char yield for this run. Yields from the two runs at 600°C (Runs 96 and 98) seem to be in reasonably good agreement with each other.

Yields of individual gases for the Balmer runs are presented in Table 14 and are shown in Figure 18. No H_2 was detected below 550°C and no CO below 600°C. The points on this graph may seem to be widely scattered but it should be noted that the entire vertical scale represents only 2% of maf coal fed, so any error will be magnified.

Pyrolysis of Forestburg and Balmer coal, among others, has been described in a thesis submitted to the University of British Columbia by Adnan Mohammed Al-Jarallah (Al-Jarallah, 1983). A spouted bed reactor was used. Coal feed rates varied from 0.5 to 8 kg/hr. Residence time based on gas spouting velocities was 0.98 seconds.

Tar yields for the two coals reported in the thesis are significantly higher than those found in this study. The maximum reported yield from Forestburg coal was 21 maf wt. % at 530°C, compared to 9.7 maf wt. % at 650°C for this study. High ash Balmer (28.5% ash) gave 12.1 maf wt. % tar at 620°C and low ash Balmer (11.5% ash) gave a maximum tar yield of 19.4 maf wt. % at 580°C in the UBC study. A maximum of 11.4 maf wt. % tar (including BTX and C_4 - C_8) is reported here for a Balmer with 8.8% ash at 650°C. A summary of the ratio of the final char weight to the bed sand weight for the Balmer tests is given in Table 15.

Table 14

Gas Yields

Balmer -149 +74 μm

N_2 atm., 0.8 sec. residence time 0.8% moisture, 8.8% ash

Temp. °C		500	550	600	600	650	700	500
Run #		95	97	96	98	93	94	58*
Yields (maf wt%)	H_2	-	0.01	0.23	0.13	0.18	0.18	-
	CO	-	-	0.23	0.20	0.42	0.32	0.08
	CO_2	0.70	0.57	0.63	0.86	1.06	0.77	0.39
	CH_4	0.29	0.64	0.87	0.59	1.56	1.46	0.31
	C_2H_4	0.03	0.07	0.08	0.06	0.12	0.12	0.04
	C_2H_6	0.11	0.18	0.22	0.16	0.33	0.30	0.12
	C_3's	0.06	0.15	0.13	0.10	0.20	0.19	0.09
	$C_1 \rightarrow C_3$	0.49	1.04	1.30	0.91	2.22	2.07	0.56
Total		1.19	1.62	2.38	2.09	3.87	3.33	1.03

* 0.49 s Residence Time

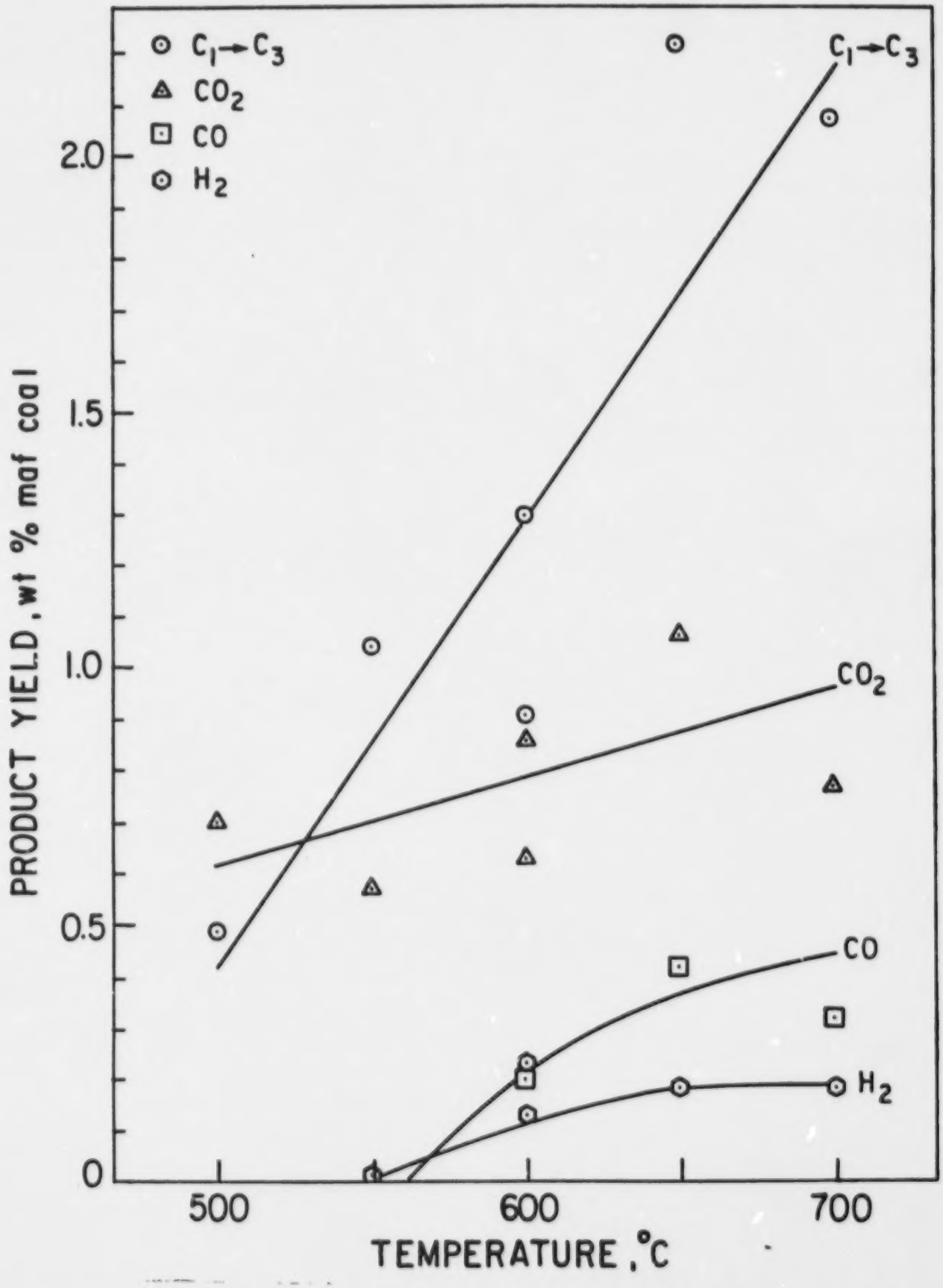

Figure 18 Gas Component Yields, Balmer Bituminous, -149 +74 μm, N_2, 0.8 S.

Table 15

Char and Sand in Reactor

Balmer -149 +74 μm

N_2 atm., 0.8 sec. residence time 0.8% moisture, 8.8% ash

Run	T (°C)	Char (g)	Sand (g)	Char/Sand
95	500	1.4	22.6	0.06
97	550	5.8	22.6	0.26
96	600	7.0	22.6	0.31
98	600	6.7	22.6	0.30
93	650	11.7	22.6	0.52
94	700	11.7	22.6	0.52

The high tar yields were claimed to be due to a low ratio of accumulated char to bed sand in the reactor at the end of a run. Al-Jarallah's results show a strong dependence of tar yield on char accumulation at constant mass of bed sand. At 500°C, Al-Jarallah reports a 35 maf wt. % tar yield at an average (that is, one half the final amount) char/sand ratio of 0.04, 8 maf wt. % at 0.2, and 3 maf wt. % at 0.6. The char/sand ratio reported in Table 15 is the ratio of final char in the reactor in kg to the amount of bed sand in kg, that is, it will be twice the corresponding value given by Al-Jarallah. Our study found a yield of 6 maf wt. % tar at 500°C at a ratio of 0.3 for Forestburg coal. Temperature was varied in the UBC study at a constant char/sand ratio of 0.2. On the basis of equivalent char/sand ratios, tar yields in our work were essentially the same as those reported by Al-Jarallah.

As a result of these observations, an attempt was made in later tests to devise a method of simulating a varying char/bed sand ratio. The results are reported later, but did not exhibit any significant increase in tar yield as the char/sand ratio approached zero.

The outstanding feature of the low volatile bituminous coal is the low gas yields, of which at least 50% are hydrocarbon gases, and the high char yields. The relatively larger (in terms of percentage of liquid product) amounts of BTX and C_4 - C_8 hydrocarbons is also of interest. The original coal contains little oxygen (about 4%), and at optimal conditions about 50% of this is rejected as CO, CO_2 and H_2O. The resulting tars, therefore, should contain little oxygen.

Elemental analysis of chars and tars are given in Table 16. An inspection of the results suggests that most of the carbon analyses, particularly for the char, must be too low. The maf C content of the char is less than that of the coal for many analyses, and the oxygen contents appear to be too high. The low C value could be due to a refractory char which was difficult to completely combust in the analytical procedure. This would lead to high ash values, which however occurred only in one analysis, the others being too low. Alternately, the char could perhaps take up oxygen readily from the air, and this would result in the low C, high O and low ash values observed. This possibility will require investigation. Run 116 is probably the most representative and the H/C ratios for char and tar at 650°C compare well with the lower rank coals. Better accuracy should exist for the tar analyses. Results show that the H/C ratio for the tar is nearly constant at about 0.94 with temperature, in contrast to tars produced from lower rank coals, which have H/C ratios decreasing with temperature.

Table 16

Effect of Temperature on Product Analysis

Balmer Coal, 0.78% Moisture, 8.77% Ash, N_2, 0.8 s.

Run	Temp °C		Analysis, weight % maf C	H	N	O	Ash	H/C
95	500	Tar	84.37	6.48	1.06	8.1		0.92
		Char	94.44	4.84	1.26	0.0	16.0	0.62
97	550	Tar	84.93	6.94	1.45	6.7		0.98
		Char	87.6	4.54	1.17	6.7	6.2	0.62
96	600	Tar	83.33	6.53	1.02	9.1		0.94
		Char	87.3	4.55	1.17	7.0	7.9	0.63
98	600	Tar	87.4	6.76	0.52	5.3		0.93
		Char	88.4	4.60	1.14	5.9	7.7	0.62
93	650	Tar	84.37	6.48	1.06	8.1		0.92
		Char	85.2	3.94	0.0	10.9	4.9	0.56
94	700	Tar	85.75	6.80	0.81	6.6		0.95
		Char	92.6	4.32	1.39	1.7	11.1 (est)	0.56
58*	500	Tar	88.7	6.9	0.9	3.5		0.93
		Char	83.6	4.1	1.3	11.0		0.59
116**	650	Tar	85.6	6.63	0.89	6.9		0.93
		Char	89.5	4.45	1.35	4.7	10.2	0.60

* 0.49 seconds residence time

** Average of two determinations; -74 +44 μm

6. MacIntyre Bituminous Coal

Pyrolysis tests were carried out with this low volatile bituminous caking coal at temperatures from 500°C to 675°C. The large reactor and a longer residence time of 0.8 seconds were used again because of the agglomeration occurring in the sand and on the reactor walls during a run.

Product yields and individual gas yields for this coal are presented in Tables 17 and 18 and Figures 19 and 20. Tar yields increased with temperature to 6.7 maf wt. % at 675°C. Higher temperatures could not be reached, for reasons discussed following.

Maximum tar and light hydrocarbon (C_4 to C_8) yields totalled 7.2 maf wt. % at 675°C, which was the maximum temperature reached. It may be that the optimal temperature for maximum liquid yield is even higher than this value.

The primary gases product was methane, showing a maximum yield of 1.9 maf wt. % at 650°C. Gas yields were low, only about one half the liquid yields, while char represented 85-90% of the products.

Temperatures indicated for these runs are only approximate, due to the highly endothermic nature of the pyrolysis reactions for this coal. This is particularly true at high temperatures, where temperatures quickly dropped by up to 50°C as coal feeding commenced (everything else constant). Temperature stability was poor (±15°C), and temperature determination became difficult as coal caked around the thermocouple. In addition to the endothermic behaviour, the cooling of the injection tube, and the use of the large reactor requiring high gas flows, contributed to limiting the maximum temperature obtainable to 675°C for this coal.

Elemental analyses of products are given in Table 19. Again, results may be questionable for some C and H values, but on the whole, the analyses appear to be more acceptable than those for the Balmer coal. If the char picks up oxygen or water from the air before analysis, this would account for the nature of some of the apparently low values. However, these discrepancies do not appear to be too large,

Table 17

Product Yields

McIntyre -149 +74 μm

0.2% moisture, 6.5% ash, N_2 atm, 0.8 sec residence time

Temp. °C		500	550	600	635	650	675	500
Run #		101	103	100	102	104	99	53*
Yields (maf wt%)	Gas	0.8	2.2	3.4	3.8	3.8	3.7	0.85
	Tar	2.0	4.2	5.9	5.4	6.3	6.7	
	BTX	0.1	0.2	0.2	0.3	0.1	0.2	
	$C_4 \rightarrow C_8$	0.2	0.3	0.3	0.4	0.3	0.3	
	Tar + LHC	2.3	4.7	6.4	6.1	6.7	7.2	2.91
	Char	103.5	91.6	85.3	87.0	86.7	86.9	95.10
	H_2O	2.0	2.2	3.0	2.7	1.7	3.8	0.96
Total		108.6	100.7	98.2	99.5	98.9	101.6	99.81

LHC = Light hydrocarbons = BTX + $C_4 \rightarrow C_8$

* Small reactor, 0.45 s.

Table 18

Individual Gas Yields

McIntyre -149 +74 μm

0.2% moisture, 6.5% ash, N_2 atm, 0.8 sec residence time

Temp. °C		500	550	600	635	650	675	500
Run #		101	103	100	102	104	99	53*
Yield (maf wt%)	H_2	-	0.1	0.2	0.4	0.2	0.2	0.02
	CO	0.1	0.2	0.5	0.5	0.5	0.5	0.09
	CO_2	0.5	0.5	0.7	0.7	0.6	0.9	0.30
	CH_4	0.1	1.0	1.5	1.6	1.9	1.5	0.24
	C_2H_4	0.0	0.1	0.1	0.1	0.1	0.1	0.03
	C_2H_6	0.1	0.2	0.3	0.3	0.2	0.3	0.09
	C_3's	0.0	0.1	0.1	0.3	0.2	0.2	0.06
	$C_1 \rightarrow C_3$	0.2	1.4	2.0	2.2	2.4	2.1	0.42
Total		0.8	2.2	3.4	3.8	3.8	3.7	0.73

* 0.45 sec. residence time

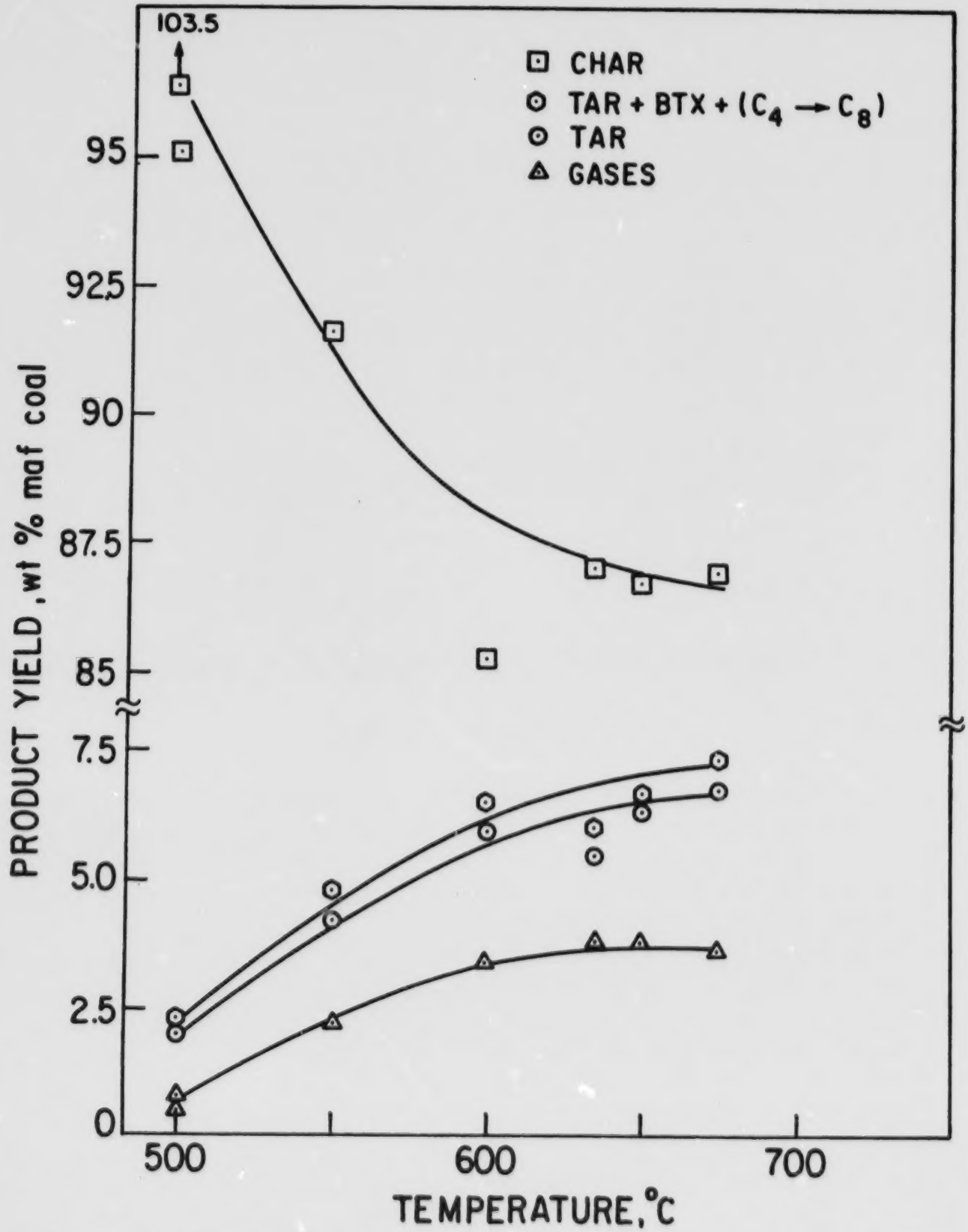

Figure 19 Char, Tar and Gas Yields, McIntyre Bituminous, -149 +74 μm, N_2, 0.8 S.

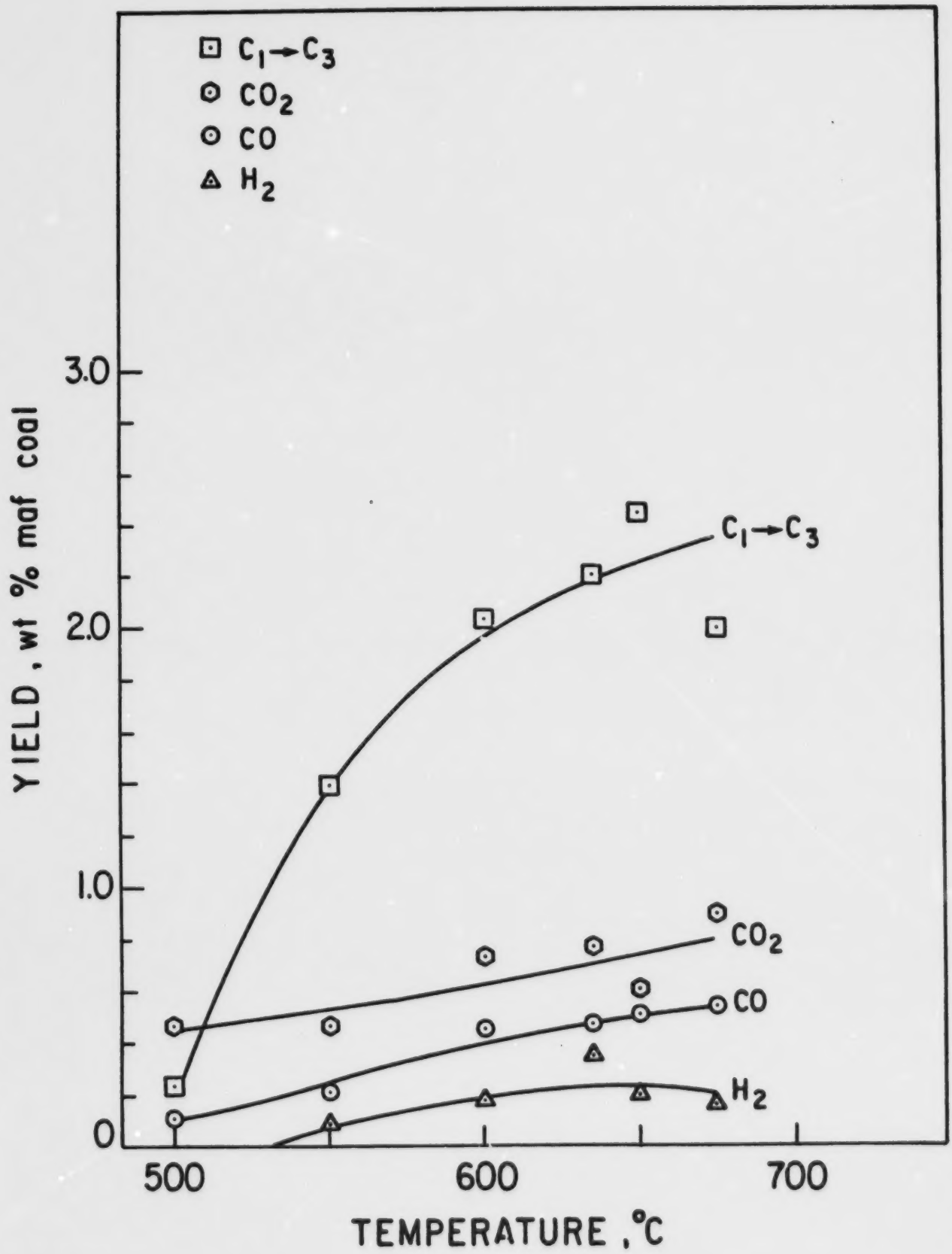

Figure 20 Gas Component Yields, McIntyre Bituminous, -149 +74 μm, N_2, 0.8 S.

Table 19

Effect of Temperature on Product Analysis

MacIntyre Coal, 0.2% Moisture, 6.5% Ash, N_2, 0.8 s.

Run	Temp °C		Analysis, weight % maf					
			C	H	N	O	Ash	H/C
101	500	Tar	88.15	6.60	0.24	5.0		0.90
		Char	85.4	4.23	0.32	10.0	6.4	0.59
103	550	Tar	87.55	6.32	0.60	5.5		0.87
		Char	86.6	4.23	0.93	8.2	7.5	0.59
100	600	Tar	85.18	6.29	0.64	7.9		0.89
		Char	89.4	4.08	1.12	5.4	6.6	0.55
102	635	Tar	87.57	6.45	1.12	4.9		0.88
		Char	89.7	4.27	0.97	5.1	9.3	0.57
104	650	Tar	86.36	6.14	0.85	6.4		0.85
		Char	88.6	4.24	0.29	6.9	9.3	0.57
99	675	Tar	84.52	6.43	0.44	8.6		0.91
		Char	87.8	4.23	1.07	6.9	7.7	0.58
53*	500	Tar	88.1	6.7	0.2	5.0		0.91
		Char	94.2	4.3	0.42	5.2	14.3	0.55

* 0.45 seconds residence time.

which may indicate a much less reactive char from the MacIntyre coal. The H/C ratio for the MacIntyre char is nearly constant, as was also the case for the Balmer coal, and has much the same value (0.57 and 0.60 respectively). The H/C ratio for the tars is also nearly constant at a value of about 0.9, only a little less than that for Balmer coal which was also nearly constant.

7. Devco Bituminous Coal

Five runs were performed using Devco coal covering the temperature range of 500° to 700°C. All runs were in the large reactor with an N_2 atmosphere and a 0.8 second residence time, because of the highly caking nature of this coal, which had the highest free swelling index of any of the coals tested (8.5).

Yields of gas, tar, C_4 - C_8 hydrocarbons, char, and water are presented in Table 20 and Figure 21. A maximum tar yield of about 17% maf wt. % appears to occur at 650° to 700°C. If the BTX and C_4 to C_8 yields are included with the tar, the yield becomes about 19% maf wt. %.

Yields of individual gases are shown in Table 21 and Figure 22. No H_2 was detected below 650°C. At high temperatures the major gaseous product was CH_4, reaching 2.4 maf wt. % of coal fed at 700°C. If hydrocarbon gases are added to the tar and light hydrocarbon yield, the total yield of tar and hydrocarbons reaches a maximum measured value of 21.3 maf wt. % of coal fed.

Overall balances for Runs 107 and 109 are less satisfactory. The high value for Run 109 may be due to an overstated char yield. The measured weight of char in the filter paper after drying was observed to change as the char cooled, possibly due to adsorption of water or oxygen onto the char. Previously, this effect was suspected but did not seem to be large and was controlled by taking weighings at a constant time after the char was removed from the oven. Chars from bituminous coals may be more hygroscopic or reactive than other chars, and as a result, in all tests after Run 109 the char was cooled in a dessicator to prevent water adsorption.

Table 20

Product Yields

Devco -149 +74 μm

0.9% moisture, 2.8% ash, N_2 atm, 0.8 sec residence time

Temp. °C		500	550	600	650	700	700
Run #		107	109	108	106	105	90
Yield (Maf wt %)	Gas	2.2	2.4	3.4	4.4	5.9	6.4
	Tar	13.4	10.0	12.8	16.6	14.7	19.7
	BTX	0.2	0.7	0.6	0.6	0.7	0.4
	$C_4 \rightarrow C_8$	0.8	0.9	1.2	1.2	1.4	1.2
	Tar & LHC	14.4	11.6	14.6	18.4	16.8	21.3
	Char	70.3	84.7	73.3	67.8	68.8	65.6
	H_2O	2.4	5.1	6.0	4.7	6.3	5.7
Total		89.3	103.8	97.3	95.3	97.8	99.0

LHC = light hydrocarbons = BTX + $C_4 \rightarrow C_8$

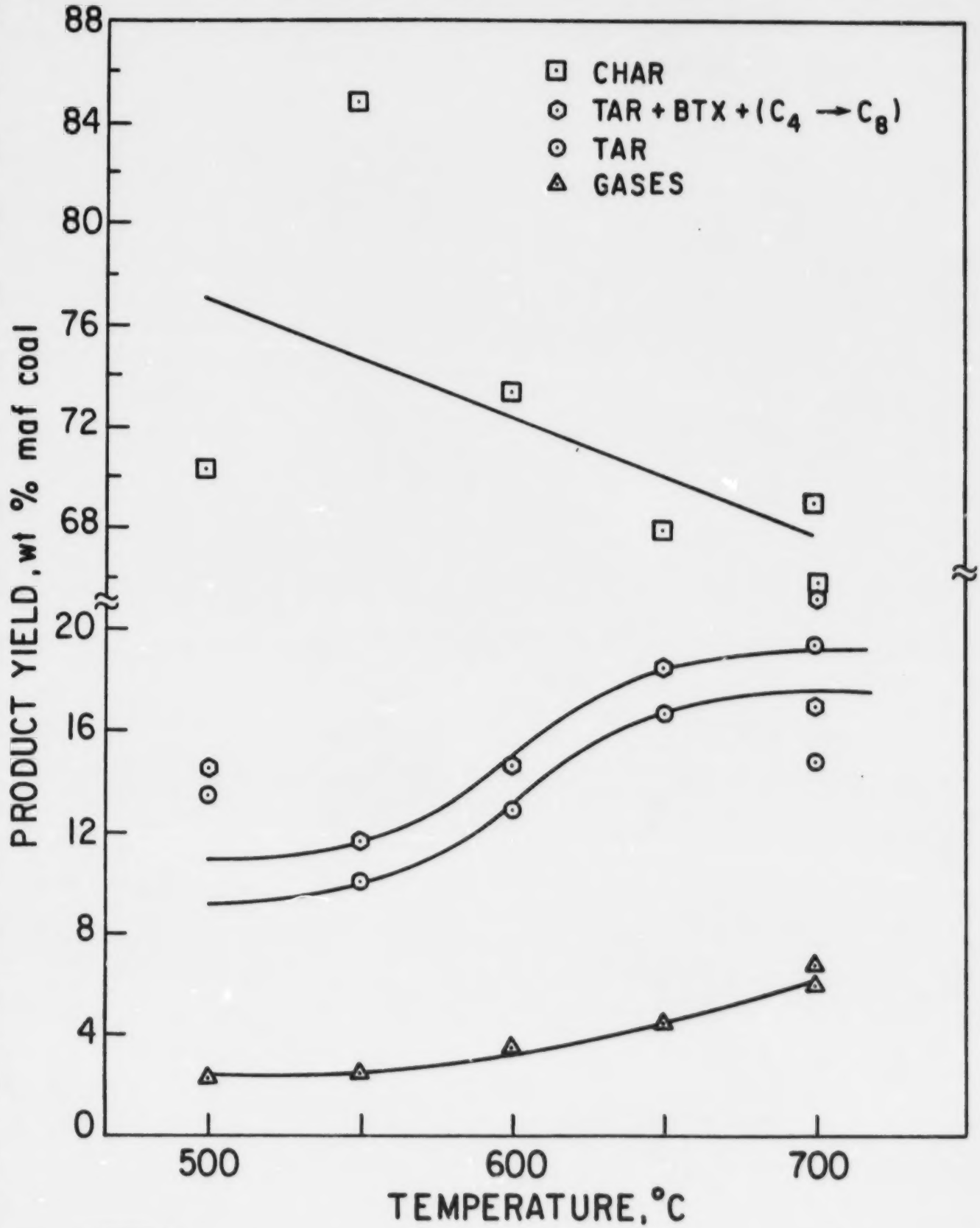

Figure 21 Char, Tar and Gas Yields, Devco Bituminous, -149 +74 μm, N_2, 0.8 S.

Table 21

Individual Gas Yields

Devco -149 +74 μm

0.9% moisture, 2.8% ash, N_2 atm, 0.8 sec residence time

Temp. °C		500	550	600	650	700	700
Run #		107	109	108	106	105	90
Yield (maf wt%)	H_2	0.0	0.0	0.0	0.1	0.2	0.2
	CO	0.3	0.3	0.5	0.7	1.2	0.6
	CO_2	0.7	0.9	1.0	1.2	1.1	1.2
	CH_4	0.7	0.7	1.2	1.5	2.1	2.4
	C_2H_4	0.1	0.1	0.1	0.2	0.2	0.4
	C_2H_6	0.2	0.2	0.3	0.4	0.5	1.1
	C_3's	0.2	0.2	0.3	0.4	0.5	0.5
	$C_1 \rightarrow C_3$	1.2	1.2	1.9	2.5	3.4	4.4
Total		2.2	2.4	3.4	4.5	5.9	6.4

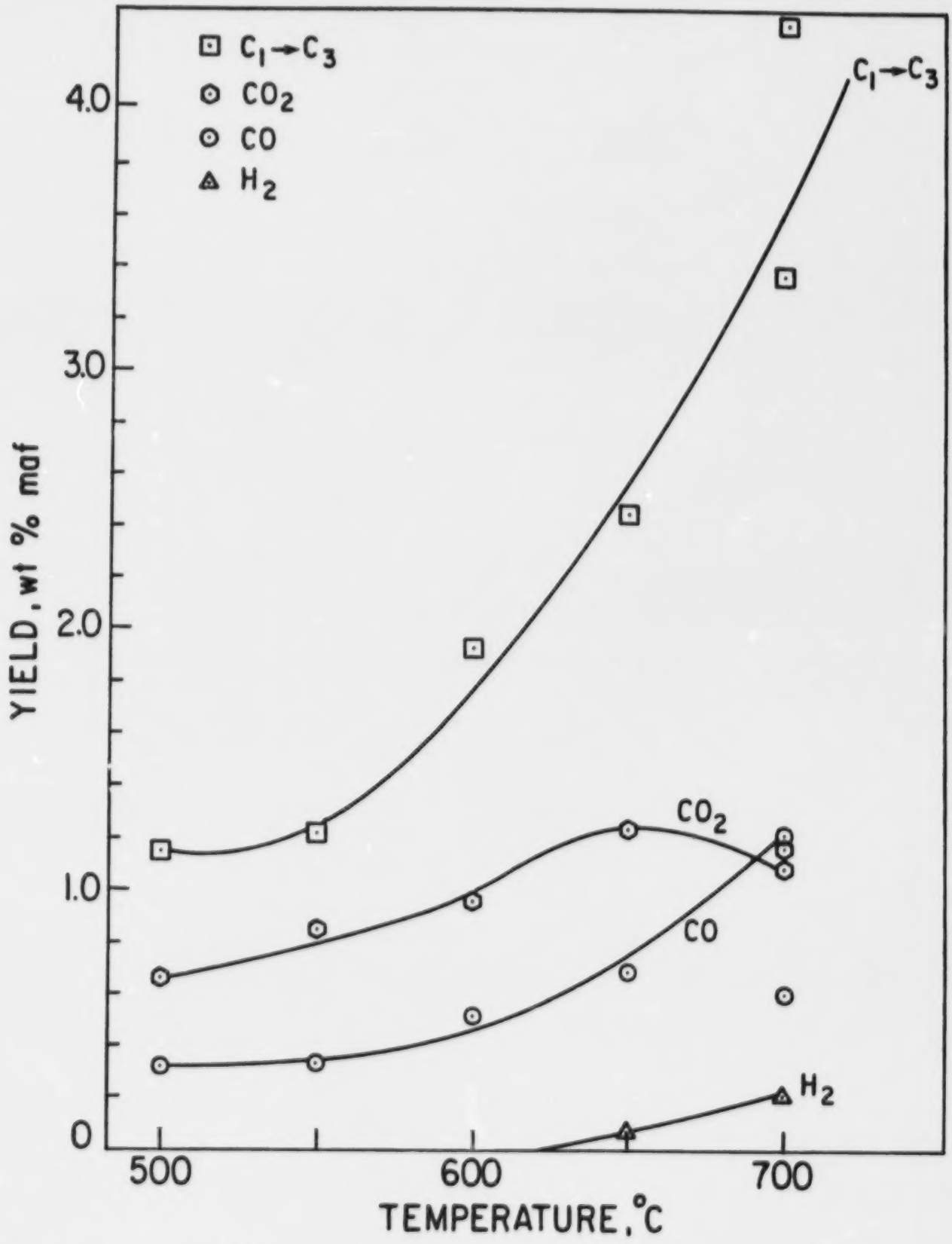

Figure 22 Gas Component Yields, Devco Bituminous, -149 +74 μm, N_2, 0.8 S.

The amounts of char retained in the bed at the end of each run are given in Table 22. The final char/sand loading was relatively low for this coal, and despite the highly plastic nature of the heated coal, it did not cause as many operational problems in the reactor as did the Balmer or MacIntyre bituminous coals with FSI of 4.0 to 4.5. In fact, it is difficult to see from these values of char/sand if there is any negative relationship to tar yield, as has been claimed (Al-Jarallah, 1983). Indeed, Run 106 has one of the higher tar yields as well as a higher char/sand ratio.

Elemental analyses of products is given in Table 23 for three runs. Again, some inconsistencies in individual values may be present in the char analyses. However, if these are due to oxygen uptake, which is a real possibility since weight gain by the char during filtering and drying were observed with this coal, the H/C ratios should not be affected. The char H/C ratios show a decrease as temperature increases, from 0.57 to 0.39, which is very similar to the values and behaviour shown by the lower rank coals. On the other hand, the H/C ratio for the tar is approximately constant as it was for other bituminous coals at 1.00 to 1.08, which is somewhat higher than the tar H/C ratios for MacIntyre or Balmer coals.

Considering the high yields of tar, the higher H/C ratio of the tar and its low oxygen content, the Devco coal appears to be a very promising feed for a pyrolysis process for the production of liquid hydrocarbons. Further work is warranted with this coal or other high volatile bituminous coals. This has also been the experience of Autralian workers using high volatile bituminous coals in a fluidized bed reactor (Smith, 1981).

Table 22

Amount of Char in the Bed
Devco -149 +74 μm
0.9% moisture, 2.8% ash, N_2 atm, 0.8 sec residence time

Temp (°C)	Run	Char in Bed (g)	Total Char (g)	% Char in Bed	Char/Sand
500	107	4.15	6.41	64.7	0.28
550	109	4.71	8.94	52.7	0.40
600	108	4.43	5.11	86.7	0.23
650	106	6.61	6.73	98.2	0.30
700	105	5.19	5.48	94.7	0.24

Table 23

Effect of Temperature on Product Analysis

Devco Coal, 1.2% Moisture, 2.9% Ash, N_2, 0.8 s.

Run	Temp °C		Analysis, weight % maf					
			C	H	N	O	Ash	H/C
88	650	Tar	80.8	7.27	1.24	10.7		1.08
		Char	81.5	3.88	1.60	13.0	3.6	0.57
89	700	Tar	81.0	6.78	1.35	10.9		1.00
		Char	85.7	2.92	0.29	11.1	4.0	0.41
90	700	Tar	79.7	6.81	2.07	11.4		1.03
		Char	83.7	2.70	1.42	12.2	6.4	0.39

8. Sukunka Bituminous Coal

Three runs were carried out using Sukunka low volatile bituminous coal from a sample supplied by the Energy Research Laboratories, CANMET. Table 24 shows the analyses of this coal with values taken from various sources. The variability of the ash content of this coal among the various analyses is interesting. However, on a dry ash-free basis, a reasonable agreement is obtained, although elemental C appears to be a bit high in the UBC sample and therefore the oxygen and the H/C ratio values are somewhat low.

Table 25 gives the results of three pyrolysis tests, one at low temperature (533°C) and two near the temperature for maximum liquid yield from bituminous coals (650°C - 700°C). Although the free swelling index of this coal is given as 3.0, 4.5 and 7.0 depending on the sources, it was found to be one of the most difficult in our experience to feed and pyrolyze in a fluidized bed. A high degree of agglomeration took place both in the sand bed and on the reactor walls; and although some variations in procedure were tried, these met with little success. As a result, the runs were difficult to complete, and a number of tests did not yield complete data. The values in Table 25 indicate a maximum tar yield of 12.16% with a 96.5% recovery at the highest temperature of 680°C. This yield is of the same order as that obtained from other low volatile bituminous coals, e.g. Balmer, and agrees with that to be expected from the correlation for bituminous coals given by Smith, (1981) which was developed at CSIRO.

This CSIRO correlation, which relates the tar yield at optimum conditions (600°C in the Australian work, but 650°C - 700°C in our tests) to the H/C ratio of the coal, is reproduced as Figure 23. Shown on this plot are the maximum yields obtained in our tests from the four bituminous coals used. Within the scatter of the correlation, the results from the present work agree well, although they are raw experimental points and have not been adjusted in any way.

Table 24

Properties of Sukunka Coal

Proximate Analysis, %

	Moisture	Volatiles		Fixed Carbon		Ash
	As is	As is	DAF	As is	DAF	As is
Furimsky*	1.90	24.0	25.3	70.7	74.5	3.2
UBC**	1.08	20.6	24.0	65.14	76.0	13.18
Waterloo	1.88	21.1	23.7	69.9	78.4	9.00
EMR***	1.79	21.15	25.7	61.68	74.3	15.98

Ultimate Analysis, DAF basis

	C	H	S	N	O	H/C
Furimsky	88.51	4.95	0.53	1.37	4.6	0.67
UBC	89.98	4.53	0.69	1.75	3.1	0.60
EMR	86.2	4.71	0.68	1.58	4.4	0.66
Waterloo	89.69	4.55	N.D.	1.84	3.9	0.61

* E. Furimsky, R. Belanger and J. Jorgensen, "The Pyrolysis of Canadian Coals for the Production of Fuels and Petrochemicals", Workshop on Pyrolysis, Fredricton, Jan. 5th, 1981.

** Ph.D. thesis of Al. Jarallah, Dept. of Chemical Engineering, University of British Columbia, 1983.

*** EMR Energy Research Laboratories, CANMET, Ottawa, Analysis of Jan. 1984, of sample supplied by M. Skubnik.

Table 25

Product Yield, Sukunka Coal

Ash 9.00%, Moisture 1.88%, N_2 atmos.

Run	143	146	145
Temperature °C	533	666	680
Particle size, µm	-595 + 250	-1195 + 595	-595 + 250
Approx. Vapour Residence Time, sec.	0.50	0.35	0.50
Yields, % by weight, maf			
Gases	3.30	4.51	5.70
Tar	4.81	8.84	13.64
Water	0.0	N.D.	N.D.
Char	92.85	77.39	78.78
Total Recovery	100.96	90.74	98.12
Gas Yields, % by weight, maf			
H_2	0.10	0.22	0.30
CO	0.29	0.46	0.73
CO_2	1.37	0.85	0.93
CH_4	0.92	1.93	2.55
C_2H_4	0.08	0.17	0.22
C_2H_6	0.24	0.38	0.45
C_3's	0.18	0.22	0.29
C_4+	0.16	0.21	0.22

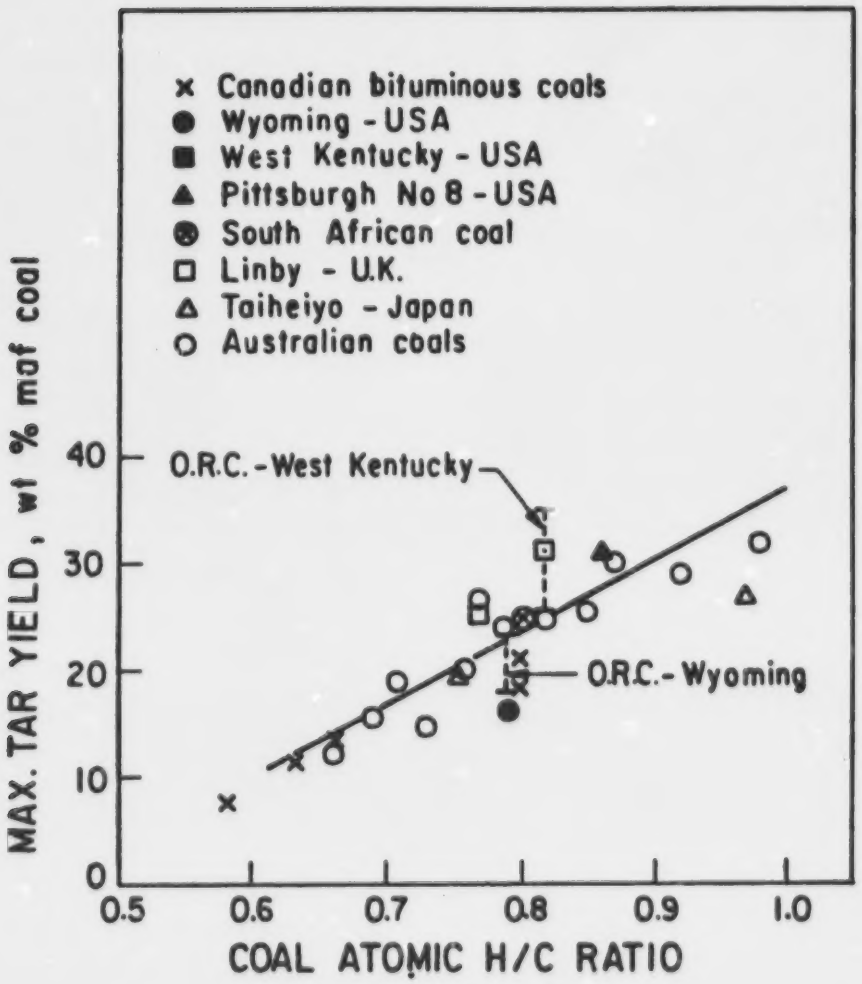

Figure 23 CSIRO Correlation of Maximum Tar Yields with Coal H/C Ratio for Biruminous Coals (from Smith, 1981), showing present results for Canadian Bituminous Coals.

Effect of Particle Size Variation

Pyrolysis tests in which particle size was varied were carried out for three coals - Saskatchewan lignite, Forestburg sub-bituminous and Balmer bituminous. Two standard feed sizes were used, -149 +74 μm (-100 +200 mesh) and -74 +44 μm (-200 +325 mesh), so that the mean feed particle diameter varied by a factor of about 2. All runs were done at conditions close to those giving maximum liquid yield.

Table 26 shows the effect of changing particle size from -100 +200 to -200 +325 mesh for Saskatchewan lignite and Forestburg sub-bituminous coals. For the lignite, gas yields decreased 5-6% and tar yields decreased 0.5 - 1.0% for the smaller particle size. Char yields increased, but may not be as high as indicated. The char samples were dried in a 110°C oven for one half-hour before weighing, which is the procedure for drying the -100/+200 mesh particle size. However, the -200/+325 mesh particle size forms a more coherent mass of char which may not have dried completely in this time. This would also account for the overall mass balances being over 100%. It is also possible that the more finely divided char gained weight through oxidation, especially as the lignite char is known to be very reactive.

The Forestburg sub-bituminous coal showed a decrease in gas yield of 7 - 8% and a decrease in tar yield of 0.5 - 1.5% as particle size was reduced. In this case, the char was allowed to dry for one hour. The char yield increased by 10 - 12%.

The lower gas and tar yields and higher char yield are probably an effect of residence time. Although the residence time based on superficial gas velocities was the same for both particle sizes, it is expected that the actual residence times for the coal particles themselves were different. The lighter -200/+325 mesh particles would probably have a lower residence time than the larger -100/+200 mesh particles, inasmuch as a larger proportion would be easily swept from the reactor after some weight loss or attrition.

Table 26

Effect of Particle Size

N_2 atm, type 1 reactor
0.45 sec residence time

Run		61	68	66	69	46	40	75
Coal		SASK LIG	SASK LIG	SASK LIG	SASK LIG	FOREST	FOREST	FOREST
Moisture (%)		7.0	7.0	7.0	7.0	9.2	9.2	9.6
Ash (%)		9.1	9.1	9.1	9.1	6.7	6.7	6.5
Temp. (°C)		650	650	600	600	650	650	650
Mesh Size		-100 +200	-200 +325	-100 +200	-200 +325	-100 +200	-100 +200	-200 +325
Yield (maf wt%)	Gas	13.9	9.1	13.8	7.6	17.6	16.6	9.4
	Tar	9.4	8.5	8.4	7.8	9.5	8.5	8.0
	Char	61.9	75.3	67.8	82.6	58.5	64.3	73.9
	BTX	0.4	0.2	0.4	0.1	0.3	0.4	0.2
	H_2O	9.2	9.3	8.3	9.9	-	-	1.5
	Total	94.8	102.4	98.7	108.0	85.9	89.8	93.0

Table 27 presents the individual gas yields as a percent of total coal fed. This table shows that the decrease in total gas yield was a result of decreased yield of all the components, and not of major changes in their relative amounts. Perhaps more useful is Table 28, which shows the individual gas yields as a percent by weight of the total gas produced. The -200/+325 mesh feed seems to produce a gas 2 - 10% richer in CO_2 and 1 - 2% leaner in H_2, 0.5 - 6% leaner in CO and 1 - 3% leaner in CH_4 than the -100/+200 mesh feed. This is particularly noticeable with the Forestburg coal. This coal produced a relatively dense char, and therefore the smaller char particle size would mean a considerable difference in the amount of char more readily blown from the bed, which was, in fact, experimentally observed. The relative increase in the ratio of CO_2 to hydrocarbon gases and to hydrogen, as well as the decrease in total gas yield, both indicate less severe heating for the smaller particles, which is consistent with a reduced particle residence time.

It is probable that an optimum particle size exists for each coal and for each type of reactor, such that heating of the particle and generation of volatiles is reasonably complete, but char does not accumulate unduly or remain for too long in the actual reaction zone. This size is probably most easily determined experimentally in each case.

The effect of particle size on yields obtained from the Balmer coal is shown in Table 29 by comparing Runs 93 and 116. In this case also, the smaller particle size gives a lower gas yield, a lower tar yield and an increased char yield. These facts, together with the decreased yield of BTX, all indicate an insufficient residence time for the smaller solid particles, inasmuch as the apparent gas residence times were identical.

In summary, the conditions for optimal pyrolysis yields will be a function of particle size and reactor type, as well as of other variables such as temperature and residence time. As a consequence, particle size must be treated as one of the basic variables of the pyrolysis system.

Table 27

Gas Yield by Component
Changing Particle Size

N_2 atm, type 1 reactor, 0.45 sec. residence time

Run		61	68	66	69	46	40	75
Coal		SASK LIG	SASK LIG	SASK LIG	SASK LIG	FOREST	FOREST	FOREST
Temp. (°C)		650	650	600	600	650	650	650
Mesh Size		-100 +200	-200 +325	-100 +200	-200 +325	-100 +200	-100 +200	-200 +325
Yield (maf wt%)	H_2	0.4	0.0	0.3	0.0	0.3	0.3	0.0
	CO	2.7	1.8	2.6	1.1	5.0	4.8	2.1
	CO_2	9.1	6.2	9.3	5.9	10.1	9.5	6.3
	CH_4	0.9	0.5	1.0	0.3	1.3	1.2	0.5
	C_2H_4	0.3	0.2	0.2	0.1	0.3	0.3	0.2
	C_2H_6	0.2	0.1	0.2	0.1	0.2	0.2	0.1
	C_3	0.3	0.3	0.2	0.2	0.4	0.2	0.2
	Total	13.9	9.1	13.8	7.7	17.6	16.5	9.4

Table 28

Gas Yield by Component
Changing Particle Size
Percent of Total Gas Produced

N_2 atm, type 1 reactor, 0.45 sec. residence time

Run		61	68	66	69	46	40	75
Coal		SASK LIG	SASK LIG	SASK LIG	SASK LIG	FOREST	FOREST	FOREST
Temp. (°C)		650	650	600	600	650	650	650
Mesh Size		-100 +200	-200 +325	-100 +200	-200 +325	-100 +200	-100 +200	-200 +325
Yield (wt% of total gas produced)	H_2	2.7	0.4	2.1	0	1.9	1.6	0.4
	CO	19.8	19.3	18.8	14.0	28.4	29.1	22.7
	CO_2	65.7	67.9	67.7	77.6	57.4	57.6	66.6
	CH_4	6.6	5.5	6.9	3.9	7.4	7.5	5.0
	C_2H_4	2.1	2.5	1.4	1.4	1.6	1.9	2.0
	C_2H_6	1.2	1.5	1.4	1.0	1.2	1.4	1.3
	C_3	1.9	2.7	1.7	2.0	2.0	0.9	2.0

Table 29

Effect of Residence Time and Particle Size

Balmer Bituminous

650°C, N_2 atm, 0.8% moisture, 8.8% ash

Run		110	93	111	116
t (sec)		1.4	0.8	0.45	0.8
Feed Size		-100/+200	-100/+200	-100/+200	-200/+325
Yields (maf wt%)	H_2	0.2	0.2	0.4	0.1
	CO	0.7	0.4	0.8	0.3
	CO_2	1.1	1.1	1.8	0.7
	CH_4	2.0	1.6	1.2	1.3
	C_2H_4	0.2	0.1	0.1	0.1
	C_2H_6	0.4	0.3	0.3	0.3
	C_3	0.3	0.2	0.2	0.2
	Gas	4.9	3.9	4.8	3.0
	Tar	9.2	10.0	10.7	6.2
	BTX	0.4	0.4	0.4	0.2
	$C_4 \rightarrow C_8$	0.6	1.0	0.7	1.1
	Char	77.8	80.7	76.8	82.0
	H_2O	4.5	1.0	4.9	2.6
Total		97.3	97.8	98.2	95.1

Effect of Residence Time

Residence times were varied for two coals, the Saskatchewan lignite and the Balmer bituminous coal. The nature of the fluid bed reactor limits the range of gas residence times which can be used and still obtain satisfactory fluidization in a single reactor. In fact, to cover the maximum range of 0.2 to 1.4 seconds attained in these tests, two reactors, one larger than the other, had to be used as explained previously.

Residence time for Saskatchewan lignite -100/+200 mesh was varied from 0.2 to 1.4 seconds. The results of these runs are presented in Table 30. It can be seen that longer residence times produce more gas and less tar. The "residence time" used here is based on the net empty reactor volume divided by the inlet volumetric gas flow rate at reactor conditions. It is difficult to separate this gas residence time from the effect of char particle residence time. Included in Table 30 is data showing the percentage of the char remaining in the fluid bed at the end of a run. It is possible that the presence of char particles remaining in the bed throughout the run may have some effect on product yields in addition to any effects caused by superficial gas residence time. However, if there is any such effect of char accumulation, the data given in Table 30 suggests it must be a minor influence.

It is clear from Table 30 that shorter residence times favour tar production. The results of Run 86 indicate that the optimal residence time for tar production may not be at the usual residence time of 0.45 seconds used in these studies. The results given in Table 30 are shown plotted in Figure 24, for the tar, and the tar + BTX. For the lignite coal, the shortest residence time of 0.2 seconds is clearly the best in terms of maximum liquid yield for the -149 +74 μm particle size used. The BTX fraction increases with longer heating time, and presumably more cracking, of the primary tar product, so that some of the loss of tar yield at longer times appears as incremental BTX product. However, about 15% of the tar is lost, mainly as additional gas product as reaction time increases from 0.2 to 1.4 seconds.

Table 30

Effect of Residence Time at 650°C

Saskatchewan Lignite -149 +74 μm

N_2 atm, 7.6% moisture, 8.8% ash

		Large Reactor			Small Reactor	
Run		81	82	84	91	86
Residence Time (sec)		1.4	0.8	0.45	0.45	0.2
Yields (maf wt%)	Gas	20.0	16.7	14.6	19.0	15.6
	Tar	7.2	7.7	8.4	8.1	9.1
	Char	61.3	64.3	63.7	64.1	66.8
	BTX	0.7	0.9	0.5	0.5	0.3
	H_2O	4.8[1]	4.6[1]	4.6[1]	5.9	6.6[2]
	$C_4 \rightarrow C_8$	1.8	-[3]	1.9	1.8	1.6
Total		95.9	94.0	93.5	99.4	100
Total Org. Liq. (maf wt %)		9.7	10.2[4]	10.8	10.4	11.0
% of Char in Bed		39.6	2.7	1.2	30.9	0

1 - estimated

2 - by difference

3 - not determined

4 - excluding $C_4 \rightarrow C_8$

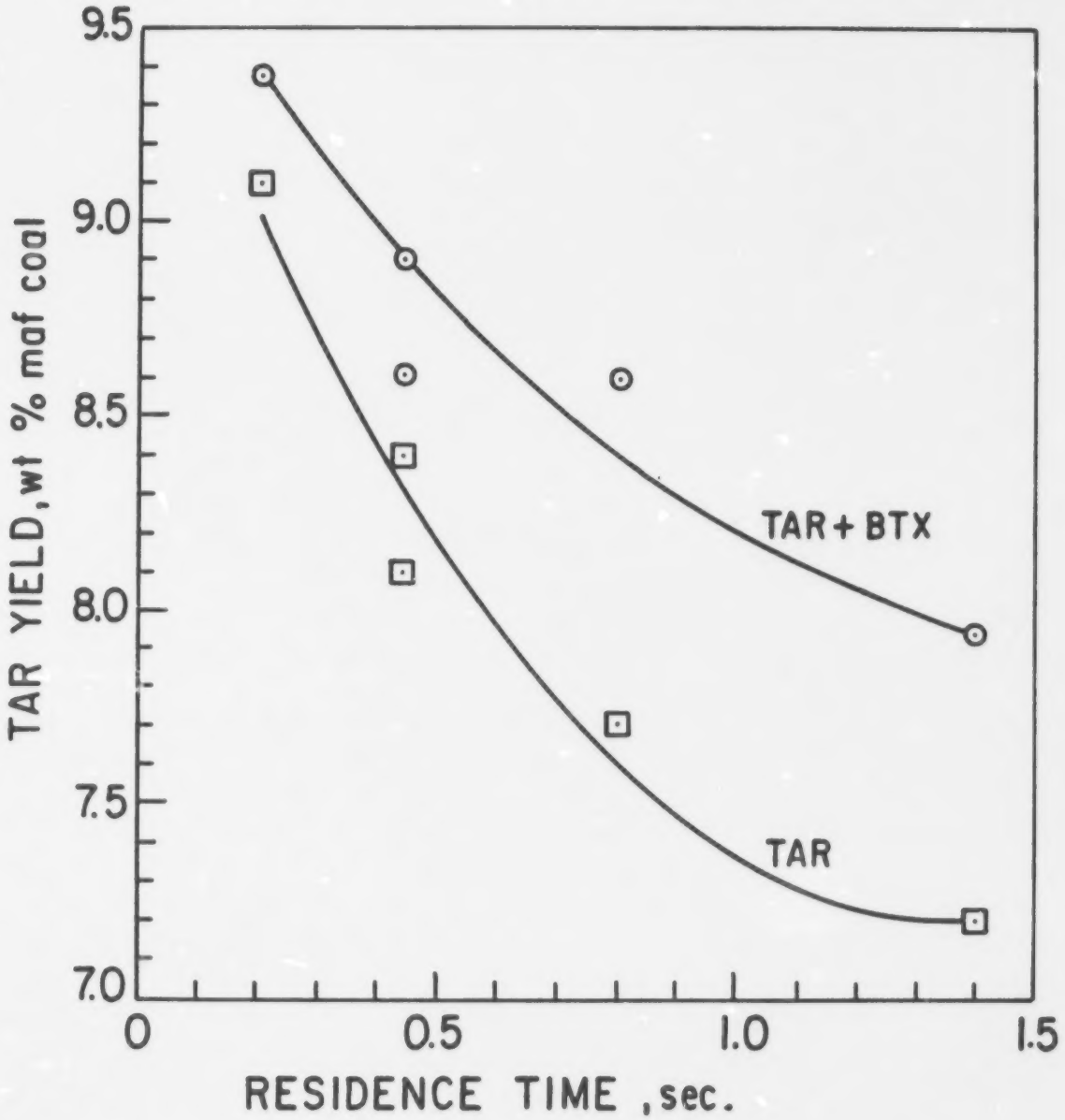

Figure 24 Effect of Residence Time on Tar Yields, Saskatchewan Lignite 3, -149 +74 μm, N_2, 650°C.

There was considerable difficulty in obtaining the results reported in Run 84. The -60/+100 mesh Ottawa sand was blown from the bed on the first attempt, so a -30/+60 mesh sand was used in subsequent attempts. The Teflon reactor outlet tube melted on the second attempt, so a metal tube was constructed. The third attempt (Run 83, not reported) was successful, but when the washed char in the filter paper was dried at 105°C, it proved to be very reactive and caught fire and burned in the oven. Close attention was paid to the char drying for Run 84. The char was again very reactive, but was dried under a covered watch glass. This high degree of reactivity was not encountered for any other run except at this particular set of conditions.

Comparing Runs 84 and 91, it can be seen that the two reactors used gave very similar results at the same conditions, except in terms of gas yields. Individual gas yields for all the runs are presented in Table 31. While the light hydrocarbon yields for Runs 84 and 91 were similar, the H_2, CO and CO_2 yields were quite different. Run 91 compared well with Run 81 in terms of H_2, CO and CO_2 yields. Runs 81 and 91 also were the runs in which a significant fraction of the char remained in the bed (30-40%). It is possible, then, that H_2, CO and CO_2 yields are more dependent on the actual char particle residence time than on gas residence time based on superficial velocities. At 650°C, if the char had a catalytic effect, then the yields of H_2, CO and CO_2 could be affected either by the action of the water gas shift reaction, or by the char acting as a gasification catalyst. Inasmuch as the lignite is known to contain alkaline earth cations, and because all of the yields of CO, CO_2 and H_2 increase for Runs 81 and 91, the latter alternative is the more likely.

The results of residence variation with Balmer coal feed are shown in Table 29 over the range of 0.45 to 1.4 seconds (Runs 111, 93 and 110). Again, the highest yields of tar and of total hydrocarbon liquids were obtained at the shortest apparent gas residence time, although the residence time effect is less pronounced. Tar yield decreases by about 14% as residence time increases from 0.45 to 1.4 seconds. The only other clear trend is an increase in light hydrocarbon gases (C_1 to C_3) as residence time increases, apparently at the expense of tar product. Apparently, for both the lignite and bituminous coals, the minimum gas residence time is preferable, at least down to probably 0.2 seconds.

Table 31

Individual Gas Yields, Varying Gas Residence Time

Saskatchewan Lignite -149 +74 μm

N_2 atm, 7.6% moisture, 8.8% ash

		Large Reactor			Small Reactor	
Run		81	82	84	91	86
Residence Time (sec)		1.4	0.8	0.45	0.45	0.2
Yields (maf wt%)	H_2	0.7	0.2	0.1	0.6	0.3
	CO	4.0	3.6	3.1	4.1	3.4
	CO_2	12.5	10.4	9.2	12.3	10.0
	CH_4	1.5	1.2	1.0	1.2	1.0
	C_2H_4	0.6	0.6	0.6	0.3	0.4
	C_2H_6	0.2	0.2	0.2	0.2	0.2
	C_3's	0.5	0.5	0.5	0.3	0.3
	Total	20.0	16.7	14.6	19.0	15.6

Effect of Quenching

Quenching was carried out by admitting a flow of cold gas into the reactor freeboard space just above the surface of the fluid bed. The small reactor was used with a total initial gas flow of 1000 ml/min (STP), consisting of 500 ml/min of fluidizing gas and 500 ml/min of gas carrying in the entrained particles of coal feed. Operated in this fashion, quenching should lead to more rapid cooling of vapour products while not affecting the fluidization behaviour or the retention of coal particles in the bed. However, because of the higher gas velocities in the freeboard space, any solid particles ejected from the bed would be much more rapidly swept out. In addition, larger particles which might otherwise fall back into the bed would also be swept out.

Saskatchewan lignite coal was pyrolyzed at 650°C with two quenching rates, 500 and 700 ml/min. The overall yields for these runs are presented in Table 32. It appears that quenching increased gas and water yields and decreased tar yields. Gas yields rose by 3-5%, water yields rose by about 2%, and tar + BTX yields fell by 1.0%, that is, 10% less tar was produced. Char yields were essentially constant.

The reasons for these results are not entirely clear. It is possible that recombination or condensation reactions in the gas phase are more important than originally believed. It is more likely that this is largely a residence time effect with respect to the solid particles, that is, the quench reduces the effective reaction time for the solids, especially in the freeboard space.

Table 33 shows the gas yield by component. The right-hand side of Table 32 shows the composition of the pyrolysis gas on a weight basis and on an N_2 free basis. The composition of the gas produced did not change significantly when quenching was introduced, which suggests that the nature of the reactions proceeding were not affected, but only their degree.

Table 32

Effect of Quenching

Saskatchewan Lignite -149 +74 μm

7.0% moisture, 9.1% ash, N_2 atm, 0.45 sec. residence time

Run		61	79	80
Temperature (°C)		650	650	650
Quenching Rate (ml/min)		0	500	750
Yields (maf wt %)	Gas	13.9	19.0	17.3
	Tar	9.4	8.5	8.1
	Char	61.9	60.7	61.2
	BTX	0.4	0.5	0.7
	H_2O	9.2	11.3	11.5
	Total	94.8	100.0	98.8

Table 33

Individual Gas Yields, Quenching Runs

Saskatchewan Lignite -149 +74 μm

7.0% moisture, 9.1% ash, N_2 atm, 0.45 sec. residence time

	Yield (maf wt % of feed)			Yield (wt % of gas produced)		
Run	61	79	80	61	79	80
Temperature (°C)	650	650	650	650	650	650
Quench Rate (ml/min)	0	500	750	0	500	750
H_2	0.4	0.5	0.4	2.7	2.6	2.3
CO	2.7	3.8	3.5	19.8	20.0	20.2
CO_2	9.1	12.8	11.5	65.7	67.4	66.5
CH_4	0.9	1.1	1.1	6.6	5.8	6.4
C_2H_4	0.3	0.3	0.3	2.1	1.6	1.7
C_2H_6	0.2	0.2	0.2	1.2	1.1	1.2
C_3	0.3	0.3	0.3	1.9	1.6	1.7
Total	13.9	19.0	17.3	100	100	100

Effect of Pyrolysis Atmosphere

Pyrolysis of Saskatchewan lignite and Forestburg sub-bituminous coals was carried out in CO_2 and H_2 atmospheres at 600°C and 650°C. Table 34 shows the effect of changing the atmosphere on pyrolysis of the Saskatchewan lignite. Pyrolysis under H_2 produced 4-12% more gas, 2-4% less tar, 6-16% more H_2O, and about 10% less char when compared to pyrolysis under N_2. The low char yield and overall balance for Run 72 indicates that some char may have been lost during the run, although no apparent loss was observed. The char largely remained in the fluid bed during the H_2 runs, so a lower char yield (compared to the N_2 atmosphere runs) is not unexpected. The presence of H_2 may promote cracking of some of the tar product, which would account for the lower tar yields. This is supported by the increase in gas yield, also. The H_2 produced is not included in the gas yields for the H_2 runs. Under a nitrogen atmosphere at these conditions, H_2 produced accounted for less than 0.5% of feed.

Pyrolysis of Saskatchewan lignite under a CO_2 atmosphere appeared to result in 3% less gas, 2% more tar, 13% more char, and 5% less H_2O than the similar N_2 atmosphere run. The gas yield for the CO_2 atmosphere is exclusive of CO_2 produced. For the corresponding N_2 atmosphere run, 9% of feed was converted to CO_2. Therefore, the actual gas yield for the CO_2 atmosphere run was probably significantly higher than the one reported here.

The results of feeding Forestburg coal under H_2 and CO_2 atmospheres are shown in Table 35. The trends are the same as those observed for the Saskatchewan lignite feed. The H_2 atmosphere produced 3-5% more gas, 1-3% less tar, and 6-12% more char. Run 27 (performed in April, 1982) is included in the table for information only. A CO_2 atmosphere produced about 8% less gas, 0.5% more tar, and 10% more char than a nitrogen atmosphere. Although water production was not measured for the N_2 atmosphere runs, the H_2O yields for the H_2 and CO_2 atmosphere runs (about 15% for H_2 and 5% for CO_2) indicate that the trend was the same as that observed for the lignite.

Table 34

Effect of Pyrolysis Atmosphere

Saskatchewan Lignite -149 +74 μm

0.45 sec. residence time, type 1 reactor
7.0% moisture, 9.1% ash

Run		61	70	78	66	72
Temperature (°C)		650	650	630	600	600
Atm.		N_2	H_2	CO_2	N_2	H_2
Yield (maf wt %)	Gas	13.9	26.5[1]	10.5[2]	13.8	17.9
	Tar	9.4	5.2	11.0	8.4	6.2
	Char	61.9	51.5	74.7	67.8	43.3
	BTX	0.4	0.4	0.1	0.4	0.6
	H_2O	9.2	15.6	4.1	8.3	22.4
	Total	94.8	99.2	100.4	98.7	90.4

1 - H_2 produced not included

2 - CO_2 produced not included

Table 35

Effect of Pyrolysis Atmosphere

Forestburg Sub-Bituminous -149 +74 μm

0.45 sec. residence time, type 1 reactor
9.0% moisture, 5.5% ash

Run		46[1]	40[1]	27[1]	73	74	77
Temperature (°C)		650	650	650	650	650	650
Atm.		N_2	N_2	50% H_2, 50% N_2	H_2	H_2	CO_2
Yield (maf wt %)	Gas	17.6	16.6	22.8[2]	20.5[2]	21.4[2]	8.9[3]
	Tar	9.5	8.5	8.0	6.9	7.3	9.5
	Char	58.5	64.3	57.6	52.1	52.8	71.5
	BTX	0.3	0.4	-[4]	0.8	0.8	0.4
	H_2O	-[4]	-[4]	18.4	15.5	15.2	5.3
	Total	85.9	89.8	106.8	95.8	97.5	95.6

1 - 9.2% moisture, 6.7% ash for runs 27, 40, 46

2 - H_2 produced not included

3 - CO_2 produced not included

4 - values not measured

Tables 36 and 37 present the individual gas yields for the H_2 and CO_2 atmosphere runs. For the hydrogen runs, CO, CH_4, and CO_2 yields increased and C_2 and C_3 hydrocarbons remained essentially the same. A CO_2 atmosphere appeared to promote CO production and decrease H_2 production. However, the low water content suggests that this change was not due to the water gas shift reaction. Light hydrocarbons (C_2 and above) were essentially the same in all atmospheres.

Table 38 gives the results of pyrolysis of Balmer and Devco coals as pyrolysis atmosphere was changed. Runs at the same temperature in an N_2 atmosphere are included for comparison.

Pyrolysis of Balmer coal in an H_2 atmosphere (Run 112) gave a tar yield of 6.8%, and a tar, BTX and C_4 to C_8 yield of 7.7%. This is a decrease of 3.7% when compared to the tar, BTX and C_4 to C_8 yield from pyrolysis in an N_2 atmosphere. The char yield and overall balance (66.5 and 82.9%) both seem low, although no experimental explanation was apparent.

Pyrolysis in a CO_2 atmosphere gave significantly higher tar yields than pyrolysis in an N_2 atmosphere. Tar yields increased 10.7 to 24.5% (that is, the tar yield more than doubled) with the Balmer coal and increased 6.5% (from 16.6 to 23.1%) with Devco coal. Tar yield could not be determined for Run 117 because an attempt was made to use cotton wool rather than glass wool as a tar filter. The cotton wool lost moisture during the run so tar yield could not be determined gravimetrically. Not all of the tar could be washed from the cotton wool.

The very high material balances made it clear that some experimental error was occurring in those runs in which CO_2 was used as the reaction atmosphere. Work by others [Tyler, (1979); Tyler, (1980); Durai-Swamy et al, (1979); Al-Jarallah, (1983)] suggested that char can act as a negative catalyst for tar production, and it was therefore assumed initially that the results shown in Tables 34-38 indicated this effect, and increased tar yields were due to deactivation of char by the CO_2. However, even if this were the case, material balances in CO_2 atmospheres should have been less in error. As a result, an investigation was carried out to better assess the Balmer coal behaviour in CO_2 atmospheres.

Table 36

Individual Gas Yields, Changing Pyrolysis Atmosphere

Saskatchewan Lignite -149 +74 μm

0.45 sec. residence time, type 1 reactor, 7.0% moisture, 9.1% ash

Run		61	70	78	66	72
Temperature (°C)		650	650	630	600	600
Atm.		N_2	H_2	CO_2	N_2	H_2
Yield (maf wt %)	H_2	0.4	-	0.2	0.3	-
	CO	2.7	8.0	8.3	2.6	4.4
	CO_2	9.1	14.9	-	9.3	11.3
	CH_4	0.9	2.5	1.2	1.0	1.6
	C_2H_4	0.3	0.4	0.3	0.2	0.2
	C_2H_6	0.2	0.4	0.2	0.2	0.2
	C_3	0.3	0.4	0.3	0.2	0.2
	Total	13.9	26.5	10.5	13.8	17.9

Table 37

Individual Gas Yields, Changing Pyrolysis Atmosphere

Forestburg Sub-Bituminous -149 + 74 μm

0.45 sec. residence time, type 1 reactor

Run		46	40	27	73	74	77
Temperature (°C)		650	650	650	650	650	650
Atm.		N_2	N_2	50% H_2, 50% N_2	H_2	H_2	CO_2
Yield (maf wt %)	H_2	0.3	0.3	-	-	-	0.2
	CO	5.0	5.0	7.9	7.2	6.8	6.7
	CO_2	10.1	9.5	11.7	10.1	11.3	-
	CH_4	1.3	1.2	2.2	2.3	2.3	1.3
	C_2H_4	0.3	0.3	0.4	0.3	0.3	0.3
	C_2H_6	0.2	0.2	0.3	0.3	0.3	0.2
	C_3	0.4	0.2	0.3	0.3	0.4	0.3
	Total	17.6	16.6	22.8	20.5	21.4	8.9

Table 38

Effect of Changing Pyrolysis Atmosphere
BALMER (0.8% moist., 8.8% ash) and DEVCO (0.9% moist., 2.8% ash)
650°C, 0.8 sec.

Coal		BALMER					DEVCO	
Run		93	112	113	115	117*	106	114
Atmosphere		N_2	H_2	CO_2	CO_2	CO_2	N_2	CO_2
Yield (Maf wt %)	H_2	0.2	-	0.2	0.1	0.2	0.1	0
	CO	0.4	0.6	1.8	0.9	1.0	0.7	1.4
	CO_2	1.1	0.7	-	-	-	1.2	-
	CH_4	1.6	1.8	2.2	1.8	1.9	1.5	1.8
	C_2H_4	0.1	0.1	0.2	0.2	0.2	0.2	0.2
	C_2H_6	0.3	0.3	0.5	0.4	0.2	0.4	0.4
	C_3	0.2	0.2	0.3	0.2	0.2	0.4	0.4
	Gas	3.9	3.7	5.2	3.6	3.7	4.5	4.2
	Tar	10.0	6.8	24.5	20.7	- *	16.6	23.1
	BTX	0.4	0.4	0.4	0.5	0.4	0.6	0.8
	C_4-C_8	1.0	0.5	0.7	1.3	0.7	1.2	1.5
	Char	80.7	66.5	114.7	94.5	89.7	67.8	81.0
	H_2O	1.0	5.0	3.7	3.7	5.7	4.7	5.3
	Total	97.8	82.9	149.3	124.3	100.2*	95.3	115.9

* Total tar yield could not be determined for Run 117.

The possibility that char produced in CO_2 runs adsorbed CO_2 or water significantly, and thus gave too large an apparent yield was checked, but the char from the Balmer coal did not adsorb any significant amounts of CO_2 when cool. Possible oxidation of the char during filtering and drying was also a possibility, but the weight gain of the char due to this effect was much too small to account for the material balance discrepancies.

However, tests showed that raw Balmer coal exposed to one atmosphere of CO_2 pressure could adsorb between 1 and 2% by weight of CO_2 at 20°C in less than one hour. Inasmuch as a feed hopper was weighed before and after a run, the CO_2 picked up by the total coal load was weighed also, and reported therefore as a reduction in amount of coal fed. Since the amount fed was only 5% or so of the hopper contents, an error of up to 40% in the weight of coal fed could result. This is the explanation of early results of pyrolysis runs in CO_2 showing material balances of 115% - 150%. In runs after #115, the coal was preconditioned by prior exposure to CO_2 and the hopper then weighed.

Table 39 shows yields from the pyrolysis of Balmer bituminous coal in a CO_2 atmosphere. Runs 113 and 115 were reported also in Table 38 (feed not CO_2 pre-conditioned) but are given in Table 39 in normalized form. Normalized yields were calculated as follows:

$$\text{component yield} = \frac{\text{g of component recovered}}{\text{total recovery}} \times 100$$

This calculation should compensate for the weighing error caused by the adsorption of CO_2 onto the raw coal. Also the tar yields for these two runs (and for Run 114) may be exaggerated because the glass wool filters contained air when weighed before the run and CO_2 when weighed after the run. This error was also corrected after Run 115 by flushing with air before final weighing. This particular error did not occur in the hydrogen atmosphere runs because the system was flushed with N_2 before weighing for safety reasons.

Table 39

Effect of CO_2 Atmosphere

Balmer Bituminous -149 +74 μm

0.8% moisture, 8.8% ash
650°C, 0.8 sec residence time

Atm.		N_2	CO_2					
Run #		93	113[2]	115[2]	118	123	125	151
Yield (maf wt %)	H_2	0.2	0.1	0.1	0.3	0.2	0.3	0.53
	CO	0.4	1.2	0.7	0.5	0.8	0.9	3.57
	CO_2	1.1						
	CH_4	1.6	1.5	1.4	1.4	2.5	2.5	3.15
	C_2H_4	0.1	0.1	0.2	0.1	0.2	0.2	0.39
	C_2H_6	0.3	0.3	0.3	0.3	0.5	0.5	0.53
	C_3	0.2	0.2	0.2	0.2	0.3	0.3	0.48
	Gas	3.9	3.4	2.9	2.8	4.6	4.7	8.64
	Tar	10.0	16.4	16.7	13.0	9.8	8.0	8.94
	BTX	0.4	0.3	0.4	0.5	0.3	0.4	N.D.
	$C_4 \rightarrow C_8$	1.0	0.5	1.0	0.6	0.9	0.8	N.D.
	LHC[1]	11.4	17.2	18.1	14.1	11.0	9.2	
	Char	80.7	76.8	76.0	82.0	74.4	81.2	73.7
	H_2O	1.0	2.5	3.0	1.9	3.8	3.7	N.D.
	Total	97.8	100	100	100.8	96.7	98.6	91.2

[1] - LHC = light hydrocarbons = TAR + BTX + $C_4 \rightarrow C_8$

[2] - normalized, total recovered = 100%

For all other CO_2 atmosphere runs reported after Run 115, the feeder was exposed to CO_2 before weighing, and after the run, and the glass wool filters contained air when weighed before and after the run.

Results given in Table 39 (Runs 113 to 125) show that tar yields decreased as amount of exposure to CO_2 increased. Runs are shown in chronological order, and the same coal was used in the feeder for all runs. Therefore, the coal fed in later runs had had a longer exposure to CO_2. High tar yields observed in the first CO_2 runs could not be reproduced. Because of this uncertainty concerning the effect of CO_2 on tar yields, a more recent, carefully controlled test was carried out (Run 151), with results also given in Table 39. The coal was conditioned for two hours prior to the test by being exposed to a flow of CO_2 at one atmosphere absolute pressure. Every effort was made to avoid weighing or other errors due to the presence of CO_2. The results of Table 39 suggest that a fully aged coal, that is, one which has fully adsorbed CO_2, does not yield any larger a tar yield than a coal pyrolyzed at the same conditions under an inert atmosphere. It is still possible that a fresh coal, newly exposed to CO_2 and immediately pyrolyzed (not aged) may show an increased tar yield. This is an interesting possibility which requires verification in future tests.

Because of the effect of adsorption of CO_2 by the raw coal feed, which was not recognized in runs prior to #115, runs with Devco bituminous coal and lignite were repeated. Table 40 shows yields for pyrolysis of Devco bituminous and Saskatchewan lignite in CO_2 and N_2. Run 114 was reported in Table 38 also, but is given in Table 40 in normalized form. Tar yield for Devco coal was highest at 700°C, the maximum temperature attainable for this coal. This was the last of the Devco runs, so this increase, although not large, was not a result of using "fresher" coal.

Run 119, Saskatchewan lignite in a CO_2 atmosphere, showed a water yield (26.1%) and overall balance (106.7%) which seemed high. The run was repeated (Run 124) and a lower water yield (17.0%) was measured, giving an overall balance of 96.3%. Tar yield decreased slightly from Run 119 to Run 124 (7.9% to 7.1%) possibly due to CO_2 exposure.

Table 40

Effect of CO_2 Atmosphere

DEVCO (0.9% moisture, 2.8% ash) and
SASKATCHEWAN LIGNITE (7.6% moisture, 8.8% ash)
-149 +74 μm, 0.8 sec residence time

Feed		DEVCO					SASK LIG		
Atm.		N_2	CO_2				N_2	CO_2	
Temp.(°C)		650	650[2]	600	650	700	650	650	650
Run #		106	114	121	120	122	82	119	124
Yield (maf wt %)	H_2	0.1	0.0	0.0	0.1	0.2	0.2	-	0.1
	CO	0.7	1.2	0.4	0.9	1.9	3.6	7.1	6.6
	CO_2	1.2					10.4		
	CH_4	1.5	1.6	1.4	1.9	2.2	1.2	1.0	0.9
	C_2H_4	0.2	0.2	0.2	0.2	0.5	0.6	0.2	0.4
	C_2H_6	0.4	0.3	0.5	0.5	0.5	0.2	0.2	0.2
	C_3	0.4	0.3	0.4	0.4	0.6	0.5	0.4	0.4
	Gas	4.5	3.6	3.0	4.1	5.8	16.7	8.9	8.6
	Tar	16.6	19.9	16.1	16.4	19.5	7.7	7.9	7.1
	BTX	0.6	0.7	0.9	0.3	0.2	0.9	0.5	0.5
	$C_4 \rightarrow C_8$	1.2	1.3	1.6	1.1	1.1	-	1.6	1.5
	LHC[1]	18.4	21.9	18.6	17.8	20.8	8.6	10.0	9.1
	Char	67.8	69.9	65.2	71.1	61.7	64.3	61.7	61.5
	H_2O	4.7	4.6	8.9	6.9	2.7	4.6	26.1	17.0
	Total	96.3	100	95.7	99.9	90.9	94.2	106.7	96.3

[1] - LHC = light hydrocarbons = TAR + BTX + $C_4 \rightarrow C_8$

[2] - normalized, total recovered = 100%

The runs reported in Table 40 for the lignite were performed with the Lignite 3 sample, in the large reactor, and at 0.8 second residence time. Previously reported runs shown in Table 34 used the small reactor at an 0.45 second residence time, and therefore direct comparison with runs carried out in N_2 or H_2 is more difficult. However, liquid hydrocarbon yields are about the same as those obtained in N_2, but higher than those using an H_2 atmosphere.

In summary, the use of a hydrogen atmosphere appears to reduce tar yields significantly for all three coals tested - the lignite, a sub-bituminous coal and a bituminous coal. Water produced is significantly increased in all cases, as is the production of CO and CO_2. Therefore, much more oxygen is rejected in the gases, but at the expense of tar yield. A hydrogen atmosphere also increased CH_4 yields for all coals but had very little effect on C_2 or C_3 yields or on BTX yield, except possibly for the Forestburg sub-bituminous coal.

The pyrolysis of coal in a CO_2 atmosphere does not appear to have any beneficial effect in increasing tar yields if the coal has been exposed to the CO_2 before feeding. Fresh coal may show a higher tar yield, but this remains to be proven. The negative effect of char on tar yields, and the negation of this effect by deactivation of the char with CO_2 or H_2O reported by others, has been reviewed by Edwards et al (1983). Apparently if a char is not formed or heated at temperatures above 600°C - 650°C, it does not show a negative catalytic activity on tar produced. Where the char is heated by partial combustion, as in the Occidental process (Durai-Swamy et al, 1979), it is also activated when the temperature reaches 850°C - 900°C. In this activated state, the char can act to greatly reduce tar yields. In the work of Al-Jarallah (1983) in which a negative effect of char accumulation on tar yields was reported, it may be possible that the accumulated char in the spouted bed used was activated in the spout by the incoming hot gas, and thus showed more effect than would a fluidized bed. However, the question of whether or not the use of CO_2 and H_2O can increase tar yields in a fluid bed or a spouted bed is not yet completely resolved. It appears to be definite that the use of hydrogen as an atmosphere may give little benefit insofar as production of liquids is concerned.

Elemental analyses of products for runs carried out in a CO_2 atmosphere after Run 115 are shown in Table 41 for Balmer, Devco and Saskatchewan lignite coals. Comparison of the Balmer results with those given in Table 16 for 650°C suggest little effect on the tar composition due to CO_2, although the coal fully aged in CO_2 before pyrolysis appears to have a little lower H content in the tar and a somewhat lower H/C ratio. The char analysis also indicates a slightly lower H/C ratio for fully aged coal. However, results with "fresh" coal in CO_2 atmospheres suggest higher hydrogen contents result in both tar and char with resulting improved H/C ratios. These results require verification.

Comparison of product analyses in Table 41 for Devco coal with those given in Table 23 show little effect of CO_2 on tar composition, but the char composition appears to contain more H in a CO_2 atmosphere, and the char has a higher H/C ratio. Although N results are the least reliable, the char also shows a steadily decreasing N content in the range 600°C - 700°C for pyrolysis in CO_2 atmospheres.

Comparison of product analyses from Saskatchewan lignite given in Table 41 cannot be made directly with those shown in Figures 6 and 7, because of the difference in residence times.

Table 41

Effect of CO_2 on Product Analysis

Run	Temp °C	Description	Tar Analysis, % maf					Char Analysis, % maf					
			C	H	N	O	H/C	C	H	N	O	Ash	H/C
117	650	Balmer coal, -100 +74 μm	73.70	7.34	0.05	18.1	1.20	94.5	4.48	0.65	0.4	12.3	0.57
118	650	0.78% Moisture, 8.77% Ash	83.82	6.54	1.13	18.5	0.94	93.1	4.56	1.41	0.9	9.8	0.59
123	650	0.8 sec., CO_2 atmos.	83.62	6.14	N.D.		0.88	90.8	4.01	1.58	3.6	13.9	0.53
125	650		85.60	6.31	0.47	7.6	0.88	86.0	3.81	1.54	8.7	7.5	0.53
121	600	Devco coal, -100 +74 μm	80.96	7.10	0.44	11.5	1.05	82.7	4.69	1.98	10.6	1.8	0.68
120	650	0.93% Moisture, 2.84% Ash	78.56	7.42	0.36	13.7	1.13	80.6	4.16	0.62	14.6	3.1	0.62
122	700	0.8 secs. CO_2 atmos.	80.75	6.43	0.09	12.7	0.96	82.6	3.88	0.19	13.3	3.0	0.56
119*	650	Sask.Lignite 3, -100 +74 μm	76.40	7.43	1.04	15.1	1.17	67.2	2.46	1.35	29.0	8.3	0.44
124	650	7.55% Moisture, 2.84% Ash 0.8 secs. CO_2 atm.	72.51	7.19	1.56	18.7	1.19	83.6	3.04	1.55	11.2	15.5	0.44

* Poor material balance.

Tests with a Catalytic Fluid Bed

Tests were carried out using a hydrogenation-deoxygenation catalyst in the bed in place of the fluidizing sand. Fifteen grams of crushed Co-Mo-0401T (Harshaw Chemical Co.) sized to -60 +100 mesh were used as a fluid bed. The composition and properties of the catalyst are given below. The coals were tested in the catalytic reactor, both at 650°C, with a feed particle size of -100 +200 mesh. Initially, only the Hat Creek coal was to be tested, but the quality of this coal was so poor that it was decided to also carry out tests with Forestburg sub-bituminous coal to give a fairer evaluation of any catalytic effects. Apparent residence time was the standard 0.44 seconds, and a 100% hydrogen atmosphere was used.

Composition of Harshaw Co-Mo-0402T Catalyst, 1/8"

CoO	3%
MoO_3	10%
SiO_2	6%
PABD	0.95 g/cc
Crush Strength	26 pounds

Because the hydrogen at 650°C reduces the catalyst readily, the catalyst was pre-reduced and the water formed measured. This amount was then used as a correction in the runs with coal.

Results for Hat Creek coal are shown in Table 42. This coal has a very high ash content (46.4% as fed). The yields obtained with sand in a nitrogen atmosphere and with the Co-Mo catalyst in a hydrogen atmosphere are compared. On a moisture and ash free basis it is apparent that the catalyst has little effect on tar, gas or char yields. Material balances could not be completed because of difficulties with the water and ash balances. However, the composition of the product gas is interesting, because althouth the total gas yield is about the same the amount of CO_2 is much less in the catalytic reactor and the CO much greater. However, the total carbon as ($CO + CO_2$) is essentially the same. The conclusion is that the catalyst is promoting the water gas shift reaction to reduce the CO_2 content and increase the CO and H_2O content. At 650°C, the equilibrium for this reaction somewhat favours CO and H_2O production. There is also a marked increase in CH_4 production, and some increase in C_2 and higher gaseous hydrocarbons.

Table 42

Tests with CoMo-0401 T Catalyst and Hat Creek Coal

Catalyst 15 grams -250 +149 μm
Coal feed -149 +74 μm Hat Creek coal, 15.4% H_2O, 46.4% ash as fed
Reactor - Type 1, 650°C, 1 atm abs. H_2, 0.44 secs.

Yields, mass %

	Nitrogen +Sand Run 127		Hydrogen + CoMo-0401 Run 131	
	As fed	maf	As fed	maf
Char	65.22	49.26	62.67	42.59
Tar	1.70	4.45	1.54	4.03
Gas	7.65	20.04	7.60	19.90
H_2	0.153	0.40	-	-
CO	1.78	4.65	4.40	11.51
CO_2	5.11	13.37	1.83	4.79
CH_4	0.37	0.96	0.98	2.57
C_2H_4	0.099	0.26	0.07	0.18
C_2H_6	0.051	0.13	0.14	0.38
C_3	0.113	0.30	0.17	0.44

Table 43 gives similar results for the Forestburg coal. In this case, because water resulting from catalyst reduction could be allowed for, a good material balance was obtained. Compared to yields in nitrogen with sand in the bed, the Co-Mo catalyst with a hydrogen atmosphere showed only minor differences in char or total gas yield. However, a drastic decrease in tar yield resulted to only one third that from the uncatalyzed reaction. A significant increase in BTX was obtained, but not of the same order as the decrease in tar yield. The amount of water produced from the catalyzed reaction increased significantly. This behaviour again supports the promotion of the water gas reaction by the catalyst as also shown by a corresponding increase in CO and a decrease in CO_2. Since the CO increase is greater than would be expected from either the incremental amounts of CO_2 disappearing or of H_2O formed, it is possible that the steam-methane reaction or the reaction of carbon with CO_2 is also catalyzed by the Co-Mo material. Methane yield and BTX yield are both increased by the catalyst as are the amounts of C_2 + saturated hydrocarbons.

In conclusion, the Co-Mo catalyst acts to decrease liquid yields, but does increase somewhat the yield of light hydrocarbons. This catalyst also significantly alters the product gas composition, but does not affect total yields of volatile gases to any large extent.

A comparison is given below of analyses for the tar product for Runs 40 and 132, both runs at 650°C, 0.44 seconds with Forestburg coal. The yields for Run 16, given in Table 43, and for Run 40 were very similar, and reaction conditions were the same.

Tar	Run 40	C = 74.54	H = 6.83	N = 1.9	O = 16.7	H/C = 1.10
Tar	Run 132	C = 90.69	H = 6.56	N = 0.97	O = 1.8	H/C = 0.86

Although too much reliance should not be placed on elemental analyses of single samples, the above results suggest that the catalyst causes de-oxygenation of the tar. In fact, for Run 132 the results in Table 43 indicate that 95% of the oxygen in the original coal is rejected as CO, CO_2 or H_2O. It appears, therefore, that the extreme reduction in tar yield is partially compensated by the removal of oxygen from the tar (from 16% to 2%), but a severe reduction in tar yield is still caused by the catalyst action. It is suggested that other reaction conditions should be investigated to determine if better tar yields are possible, or better yields of C_2 + hydrocarbons, than obtained in Run 132, while at the same time the tar is substantially de-oxygenated.

Table 43

Tests with CoMo-0401 T Catalyst and Forestburg Coal

Catalyst 15 grams -250 +149 μm
Coal feed -149 +74 μm Forestburg sub-bituminous
10.0% moisture, 6.73% ash as fed
C 71.2% H 4.5% maf
Reactor - Type 1, 650°C, 1 atm. abs. H_2, 0.44 secs.

Yields, mass %

	Nitrogen +Sand Run 16		Hydrogen + CoMo-0401 Run 132	
	As fed	maf	As fed	maf
Char	56.12	59.31	57.02	60.39
Tar	8.74	10.50	2.58	3.10
BTX	0.24	0.29	1.06	1.27
Water	17.10	8.53	20.01	12.02
Gas	15.62	18.76	17.93	21.53
Total	97.82	97.39	98.60	98.31
H_2	0.30	0.36		
CO	4.37	5.25	8.86	10.64
CO_2	9.51	11.42	5.02	6.03
CH_4	1.00	1.19	2.76	3.31
C_2H_4	0.25	0.30	0.23	0.28
C_2H_6	0.20	0.24	0.43	0.51
C_3			0.39	0.47
C_4			0.24	0.29

Effect of Pre-Oxidation of Pyrolysis of Caking Coals

A sample of Devco coal (-100 +200 mesh) was kept in an oven with air circulation at 105°C for 27 days. This coal was then used to perform a standard pyrolysis run at 650°C, 0.8 seconds vapour residence time and in a nitrogen atmosphere. Results on a maf basis are shown in Table 44 (Run 142) compared to the results at the same conditions obtained for less strongly oxidized Devco coal, which was kept in a sealed bottle at room temperature after grinding (Run 106). The principal difference appeared to be a decreased tar yield for the oxidized coal with a corresponding increase in gas yield, this increase being almost entirely CO and CO_2. It would seem that some volatiles recovered as organic liquids from the pyrolysis of unoxidized coal now appear largely as carbon oxides and water with a corresponding loss in organic liquid yield. The oxidized Devco coal did exhibit somewhat better fluidization behaviour with much less visible agglomerates formed with the sand and less coke formation on reactor walls.

Devco coal contains both nitrogen (1.69% mf) and sulfur (1.0% mf). If these are evolved during pyrolysis in gaseous form they would not be accounted for in the material balances for any of the coals tested. Particularly, if the nitrogen was evolved as NO_x, which is quite likely, a significant loss in material balance would result. For coals such as Devco which contain significant amounts of both N and S, this factor could account for at least half the losses in the material balance.

Table 44 also gives elemental analyses for the normal and the oxidized Devco coal. As expected, the oxidized coal contains a larger percentage of oxygen. However, it also appears to have lost some hydrogen as shown by the reduced H/C ratio, possibly by loss of volatiles during the long heating period. The two tar products compare reasonably well, with only a minor reduction in hydrogen content in the tar from the oxidized coal. It would seem, therefore, that the major drawback to using an oxidized coal in order to reduce agglomeration would be the approximately 25% loss of tar yield.

Table 44

Pyrolysis of Pre-Oxidized Devco Coal

-149 +74 μm, 2.8% ash, 0.0% moisture, 0.8 sec. residence time
N_2 atmos., coal held at 105°C for 27 days before pyrolysis

	Run 106 (non-oxidized) FSI = 7.5	Run 142 (oxidized) FSI = 0
Temperature	650°C	650°C
Yields, maf		
Gases	4.4	7.6
Tar	16.6	12.8
Char	67.8	67.1
BTX	0.6	0.1
Water	4.7	4.9
$C_4 \rightarrow C_8$	1.2	N/D
Total Recovery	95.3	92.5
H_2	0.1	0.17
CO	0.7	1.80
CO_2	1.2	2.45
CH_4	1.5	1.88
C_2H_4	0.2	0.25
C_2H_6	0.4	0.38
C_3	0.4	0.33
C_4	N/D	0.30

Ultimate Analysis*	C	H	N	S	Ash	H_2O	O	H/C
Normal Devco	86.33	5.48	1.82	1.09	2.8	0.94	5.3	0.76
Oxidized Devco	82.5	4.87	1.66	1.09	2.8	0.0	9.9	0.71
Tar, Normal Devco	80.8	7.27	1.24	N/D			10.7	1.08
Tar, Oxidized Devco	80.60	6.86	1.44	N/D			11.1	1.02

* C/H/N/S/O values are maf basis.

Effect of Acid Washing of Lignite Coal

Tests were carried out to assess the effect of acid washing on tar yields from a low rank coal. It has been reported that when Victorian brown coal, which has a considerable ion exchange capacity, was washed with acid to remove alkali ions and replace them with hydrogen ions, that a very pronounced increase in tar and oil yield occurred (Tyler and Schafer, 1980).

The two low rank coals used in the present test program - Saskatchewan lignite and Hat Creek sub-bituminous - differ in their ash content. The Hat Creek coal has such a high ash content - over 40% in our sample - that the benefits from acid washing would probably be small relative to the acid usage required. Therefore, Saskatchewan lignite (our No. 3 sample) was selected for this test. Also the lignite would probably display a greater ion exchange activity which arises from the humic acid content than would the sub-bituminous coal. If the carboxylic acid groups of the humic acids, which have the ion exchange capabilities, have alkaline earth cations displacing the protons, then a negative effect on tar yields would be observed.

A sample of 250 grams of Saskatchewan lignite No. 3 (-30 +60 mesh) was treated for 60 minutes with about 500 mls of 2 N HCl. The original ash content of the lignite at 7.6% moisture was 8.8%, so a large excess of acid was present. After filtering, the coal sample was washed with about 1500 mls of water to remove residual acid. The coal was then air dried and ground in a laboratory mill to -60 +200 mesh.

This coal was used as a feed to the small pyrolysis reactor (Type 1) at standard pyrolysis conditions, that is, 1 atm pressure, 100% nitrogen atmosphere, 0.45 seconds vapour residence time in a fluidized bed containing 15 grams of -60 +100 mesh Ottawa sand. Results of pyrolysis Runs 138 - 141 are shown in Table 45, with values from Run 91 on untreated coal shown for comparison.

Comparison of results from Runs 91 and 139 show two major differences. Tar yields are much higher for the acid washed coal - nearly 60% greater. The ash-free char yield is much lower. In addition, material balances are not as satisfactory.

Table 45

Pyrolysis of Acid Washed Saskatchewan Lignite (Sample No. 3)

Screen Analysis -250 +149 μm 68.5%
-149 +74 μm 31.5%

Ash 5.15% after acid wash, 8.8% before acid wash. (Air dry basis)
Moisture 10.01% after acid wash, 7.6% before acid wash (air dry)

Run No.	91*	138	139	140	141
Temperature °C	650	650	650	600	550
Yields, % maf					
Gases	19.0	20.87	19.12	17.04	14.55
Tar	8.1	12.13	12.93	13.50	12.80
Char	64.1	51.83	52.96	56.00	58.32
Water	5.9		6.32	5.89	5.03
BTX	0.5		0.12	0.08	Tr.
Recovery	99.4		91.45	92.51	90.86
H_2	0.6	0.15	0.24	0.18	Tr.
CO	4.1	6.81	6.81	5.72	4.20
CO_2	12.3	11.76	9.38	9.05	8.76
CH_4	1.2	1.20	1.38	1.17	0.86
C_2H_4	0.3	0.47	0.48	0.25	0.17
C_2H_6	0.2	0.17	0.19	0.18	0.17
C_3	0.3	0.37	0.38	0.26	0.21
C_4→C_8	1.8		0.26 (C_4 only)	0.21	0.19

* Not acid treated.

It is possible that much of the material balance error results from overestimation of the coal feed rate. Because the feed had a somewhat higher than normal moisture content for an air-dried sample, further drying could occur in the feeder hopper. Since this hopper contains 250 grams of coal and only about 6 grams are fed in a run, a small decrease in feed moisture is reported as a sizeable error in coal fed. This was checked by determining moisture content of the coal feed before and after the runs, but the moisture loss appeared to account for only about one half the missing material. However, because the determination of all the basic products is quite reliable, an error in feed rate would allow normalization of the results. If Run 139 is normalized, tar yield would be 14.14% maf.

There is no apparent explanation for the drop in char yields. However, on a normalized basis, char yield for Run 139 is 57.9%, which is about as expected given the higher tar yield. It is interesting that total gas yields are about the same for acid treated or untreated coal. However, the gas from the acid washed coal appears to be higher in CO and lower in CO_2. The decreased H_2 yield for the acid washed coal also suggests that the water gas shift reaction proceeds to a lesser degree. If the catalytically active alkali ions have been removed, this result might be expected.

The acid washing removed about 3.7% of ash, or about 42% of the ash originally present. The increase in tar yield is very significant, and shows clearly the negative effect on liquid yields of alkali cations in the original coal ash. Further investigation of this effect, and its possible economic ramifications, appears to be warranted.

Effect of Char Accumulation

The data given in Tables 15 and 22, showing the residual char remaining in the sand bed at the end of a run, represent a fairly wide ratio of char/sand. These ratios, or the ratio of the tar produced per unit of char retained in the bed, do not appear to indicate any very strong effect of char loading on liquid yields.

An attempt was made to determine if the presence of char in the bed did inhibit liquid yields by simulating a "zero char accumulation" reactor. This simulation was achieved by operating the fluid bed reactor on alternate short pyrolysis and char combustion cycles. This approach was considered to be valid because of the very small total system volume in the reactor and feed lines, so that switch-over between two operating modes on a fairly short time cycle could be practical. After three minutes of coal feed, the coal feeder and nitrogen flow was shut off and a stream of air was introduced. The bed temperature increased by 50° - 100°C usually during the combustion cycle and then decreased. When the bed temperature had fallen to only 20° or so above the desired operating temperature, the pyrolysis cycle was restarted by starting the feeder and the nitrogen flow. Ten feeding cycles were used, to give a total pyrolysis feed time of 30 minutes.

During a run the total gas volume - pyrolysis gas as well as combustion gas - was collected. Total gas volume was determined by injection of a known amount of tracer gas into the gas bag. Water determination was by Karl Fischer titration of the solvent washings at the end of a run plus the water in the gases. At the end of a run, no char was visible in the reactor or in the bed sand which remained clean.

Two runs were carried out using the Forestburg coal, one at 650°C (Run 135) and Run 136 at 520°C (average). Results are shown in Table 46, together with earlier results of normal pyrolysis runs for comparison.

Table 46

Effect of Char Accumulation on Liquid Yields

Forestburg Sub-Bituminous, N_2, -149 +74 μm
9.85% Moisture, 7.5% Ash

Run No.	16	40	46	133	135*	136*	13
Temp. °C	650	650	650	650	650	520	500
Weight of sand, gms	15	15	15	25	15	15	15
Feed rate, grams/hr	16.7	14.8	14.8	27.9	21.7	19.9	18.5
Vapor residence time, sec	0.45	0.45	0.45	0.38	0.45	0.45	0.45
Char accumulation- % of char in the bed to the total char recovered	46.7	30.13	41.5	12.6	-	-	60.3
Yields, wt % of coal, as fed							
Gases	15.6	13.9	14.8	15.9			10.2
Tar	8.7	7.1	8.0	8.1	8.5	6.24	5.5
Char	56.1	60.8	55.9	58.1	38.1**	32.49**	64.4
BTX	0.24	0.43	0.31	0.10	-	-	-
Water	17.10			13.9	13.2	21.95	19.83
Total	97.8			96.2	-	-	100.3
H_2	0.30	0.23	0.27	0.29	0.25	0.102	0.06
CO	4.37	4.04	4.20	4.57	12.67	16.08	2.24
CO_2	9.51	8.02	8.47	8.88	59.14	82.54	6.95
CH_4	1.00	1.04	1.10	1.25	1.11	0.606	0.58
C_2H_4	0.25	0.26	0.25	0.27	0.26	0.120	0.14
C_2H_6	0.20	0.20	0.17	0.19	0.18	0.135	0.19
C_3				0.26	0.25	0.157	0.24
C_4				0.24	0.23	-	-

* Zero char accumulation runs.

** Char blown out of bed during pyrolysis cycle.

An examination of the results given in Table 46 indicates that the tar yields obtained in the "zero char accumulation" runs were just about as expected if there was no effect of the relative amount of char accumulated in the sand bed. Because of the presence of combustion gases, the only gas yields from Run 135 which can be compared are the H_2 and hydrocarbon gases. At 650°C, the yields of these gases agree closely with those obtained in runs with variable amounts of char accumulation, e.g. Runs 16 and 133. Similarly, yields of H_2, CH_4, C_2H_4, etc. from Run 136 at 520°C compare reasonably well with those from Run 13 which had a high char accumulation.

It can be concluded that the presence or absence of char in the fluidized bed does not appear to have any significant effect on tar or hydrocarbon gas yields from Forestburg sub-bituminous coal at temperatures up to 650°C. This conclusion differs from that put forward by Al-Jarallah (1983) for Forestburg coal. Perhaps the explanation may be the one offered earlier, that is, that the char in our work is never heated significantly above the pyrolysis reaction temperature, and thus never becomes "activated", whereas this may occur in other processes.

Carbon - Hydrogen Elemental Balance

Carbon, hydrogen and oxygen balances for the runs with Lignite 3 are presented in Table 47 and for examples of Forestburg and McIntyre coals in Table 48. The results are given as the percentage of a given element which was contained in the final products. In these results, the char is the major product, and as a result, any errors in char elemental analyses are reflected strongly in the final balance closure. One real problem exists in obtaining an unequivocal elemental analysis of the feed. Sampling problems are severe with heterogeneous mixtures such as raw coal, and the use of only a few milligrams of sample, as is required for the Perkin-Elmer 240C elemental analyser used. The micro-analytical technique is not ideal for heterogeneous materials. A second problem exists in obtaining good carbon analyses among coals with vastly different reactivities in combustion. As a result, carbon values for refractory coals are frequently low, and may be low also for high ash coals. The same problem exists in analysing char, although chars are generally more reactive and give better results for carbon. However, the reactive chars can adsorb water and oxygen from the air, with the result that the hydrogen content may be overstated. Again, it should be remembered that all oxygen values reported are obtained by difference, and therefore contain all the overall mass balance errors, as well as the errors due to analytical errors. Since both of these error sources are most commonly due to low values, the oxygen value is usually overstated.

Accuracy in C/H analyses has improved significantly in our laboratories since the work reported here was done. However, accurate elemental analyses are still, and will remain, a problem.

The results in Table 47 show clearly the enrichment of the tar fraction with hydrogen and the depletion of oxygen. The carbon conversion to tar is approximately the same as the tar yield, but the oxygen content is only about one half the proportionate amount that might be expected. The oxygen is rejected preferentially as CO, CO_2 and H_2O. Unfortunately, from 20% to 40% of the hydrogen is consumed to form water of reaction, so that hydrogen depletion also occurs as part of the de-oxygenation process. However, this is largely at the expense of the char. The results shown in Figure 8 also show the selective de-oxygenation of the tar fraction with the H/C ratio at all temperatures exceeding that of the dry ash free coal.

The closures of the elemental balances in Table 47 are reasonably satisfactory, with the largest errors being in the oxygen results, as expected. High hydrogen yields in the lower temperature runs under 600°C may be due to the more reactive nature of the low temperature chars with the result that some water adsorption occurred. This effect would also account for the higher errors in oxygen results for the lower temperature runs.

Table 48 compares elemental balances on an maf basis for three Western Canadian coals, a lignite, a sub-bituminous coal and a bituminous coal. The lignite pyrolysis was carried out in a hydrogen atmosphere, and possibly some hydrogen was added to the products. The very high oxygen result suggests a highly reactive char was formed in the hydrogen atmosphere, and oxygen (and perhaps also water) was picked up from the air. Results for the Forestburg sub-bituminous coal show much the same behaviour as the lignite results given in Table 47. The tar is preferentially deoxygenated, with the oxygen being rejected as H_2O, CO_2 and CO, with the hydrogen for H_2O formation coming largely from the char.

Results for the McIntyre bituminous coal are given at two temperatures, 500° and 600°C. The tar yield and carbon conversion to tar are essentially the same, however, the low temperature tar appears to contain a good deal more oxygen than the high temperature tar. The char yield is about 95% for this coal, and as a result the elemental balances depend nearly entirely on the correctness of the char analysis. As pointed out earlier, it was difficult to obtain highly accurate coal or char analyses at the time these results were obtained. Therefore, no great significance can be given to the balance results. However, they do show that the char is somewhat depleted of hydrogen, and they also suggest again that the low temperature char from bituminous coal may be much more reactive towards oxygen than is the high temperature char.

Table 49 gives results calculated from elemental analyses of the Hat Creek pyrolysis products for the runs whose data are given in Table 11. These values have been presented in Table 49 on the basis of the coal "as fed" and not on the dry ash free basis. This basis was chosen because of the high ash content of the coal, and

Table 47

Elemental Mass Balances

Saskatchewan Lignite -149 +74 μm

N_2 atm, 0.45 sec residence time

C = 71.2% H = 4.24% N = 1.64% O = 22.9% (maf basis)

Run	T (°C)	Type of Balance	(Mass of Element in Product/Mass of Element Fed) x 100					
			Gas	Tar	Char (ash-free)	BTX	H_2O of Reaction	Total
65	500	C	4.6	7.2	81.2	0.3	-	93.2
		H	6.3	10.4	60.4	-	31.3	108.4
		O	26.2	3.7	49.7	-	46.3	125.8
		Yield	9.5	6.5	72.6	0.2	11.9	100.7
63	550	C	5.9	8.4	79.9	0.3	-	94.5
		H	9.3	15.0	57.9	-	22.4	104.6
		O	31.9	4.6	40.4	-	30.0	106.6
		Yield	11.9	7.7	69.2	0.2	7.7	96.7
64	550	C	5.4	7.5	81.9	0.5	-	95.2
		H	8.7	13.0	60.9	-	30.4	101.3
		O	28.6	4.0	45.9	-	41.7	120.3
		Yield	10.7	6.9	72.1	0.3	10.8	100.8
66	600	C	6.9	9.4	80.2	0.6	-	97.1
		H	14.0	16.0	47.8	-	21.9	99.6
		O	36.1	4.4	34.6	-	32.1	107.3
		Yield	13.8	8.4	67.8	0.4	8.3	98.6
67	600	C	6.4	9.3	81.2	0.5	-	97.4
		H	11.9	16.4	50.8	-	13.4	92.6
		O	33.2	7.3	36.8	-	20.9	98.5
		Yield	12.6	9.0	69.6	0.3	5.4	96.9
61	650	C	6.9	10.7	74.8	0.5	-	92.9
		H	18.9	14.2	42.5	-	18.9	94.4
		O	35.8	5.3	31.1	-	35.7	107.8
		Yield	13.9	9.4	61.9	0.4	9.2	94.8
60	750	C	12.7	7.5	73.8	0.9	-	94.8
		H	36.9	10.6	31.6	-	-	79.0
		O	57.1	3.6	21.2	-	-	82.0
		Yield	23.5	6.8	59.3	0.6	-	90.2

Table 48

Elemental Mass Balances

Various Coals

Run	Balance	(Mass of Element in Product/Mass of Element Fed) x 100 Gas	Tar	Char (ash-free)	BTX	H_2O of Reaction	Total
52	C	5.8	7.0	84.4	0.4	-	97.6
Forestburg	H	4.5	11.4	64.8	1.1	10.2	92.0
-149 +74 μm	O	27.5	3.1	58.4	-	13.2	102.3
500°C, N_2 atm	Yield	11.1	5.8	76.0	0.3	3.8	97.1
70	C	14.6	6.0	64.1	0.6	-	85.2
Sask Lig	H[1]	18.6	9.2	37.1	-	40.2	105.1
-149 +74 μm	O	67.0	2.3	18.4	-	60.6	148.3
650°C, H_2 atm	Yield	26.5	5.2	51.5	0.4	15.6	99.2
53	C	0.6	2.8	94.0	-	-	97.4
McIntyre	H	2.5	4.3	86.9	-	2.8	96.5
-149 +74 μm	O	5.7	4.3	124.0	-	24.2	158.2
500°C, N_2 atm	Yield	0.9	2.9	95.1	-	1.0	99.9
54	C	0.5	2.0	97.8	-	-	100.3
McIntyre	H	2.2	3.0	92.2	-	4.5	101.8
-149 +74 μm	O	6.5	0.3	31.1	-	40.1	77.9
600°C, N_2 atm	Yield	0.8	2.0	95.6	-	1.8	100.2

[1] = H_2 atmosphere; not all H_2 taken into account.

Table 49

Elemental Mass Balances (see Table 11)

Hat Creek Sub-Bituminous Coal
15.4% moisture, 46.4% ash, N_2, 0.45 s., 21.7% C, 3.16% H (as fed)

Run	Temp. °C		Gas	Tar	Char	Total H_2O	Total
			Gms. of element in product/100 gms. coal as fed				
129	500	C	1.91	0.77	22.58	-	25.3
		H	0.083	0.081	1.36	1.63	3.15
		Yield	5.43	1.00	68.12	14.71	89.26
130	550	C	1.97	0.87	28.56	-	31.4
		H	0.19	0.094	1.38	1.21	2.87
		Yield	5.62	1.19	67.94	10.85	85.60
128	600	C	2.53	0.86	27.13	-	30.5
		H	0.21	0.119	1.24	1.46	3.03
		Yield	7.30	1.13	66.21	13.11	87.75
127	650	C	2.74	1.24	16.83	-	20.81
		H	0.30	0.13	0.59	1.38	2.40
		Yield	7.76	1.70	65.22	12.44	87.12
126	700	C	3.75	0.96	21.34	-	26.05
		H	0.46	0.085	0.70	1.61	2.86
		Yield	10.71	1.23	61.55	14.46	87.95

the difficulty of obtaining accurate ash values for chars. In every case but one, the carbon yield in products is too high, and the hydrogen yield too low. The reasons for these discrepancies are not clear. The high moisture content (15.4%) may not be correct for the coal actually fed to the pyrolysis reactor, inasmuch as dry gas was used to entrain the coal, and if drying of the hopper contents occurred, then more organic coal matter was contained in the feed than was assumed. This factor could account for both the high carbon recovery and low hydrogen recovery. There is a good likelihood that the carbon analysis for the feed is low, also. The results show the same behaviour as the lignite or the sub-bituminous coal, that is, oxygen is preferentially removed as CO, CO_2 or H_2O and the tar is correspondingly depleted in oxygen, as shown by the high H/C ratio of the tar. Future work with low rank coals should be carried out on relatively dry feed materials if good carbon-hydrogen-oxygen balances are desired.

Table 50 and 51 show results of elemental balances for the lignite and for Devco bituminous coal for runs carried out in a CO_2 atmosphere (see Table 40). Again, results in both tables are presented on the basis of the coal fed, and not on a dry ash-free basis. The Devco coal results gave low carbon yields, and at the two lower temperatures, overstated the hydrogen yield. There is no apparent explanation for the low carbon yield. Although CO_2 is not included in the analysis, this represented only a yield of 1.0-1.5% of the coal fed, and does not account for the low results. The most probable explanation lies in low carbon analyses for char. The char is weighed immediately after a run, but elemental analysis is carried out some time later. If the char gains weight due to oxygen or water adsorption during this interval, this weight gain is not taken into account, and would result in low C values and high H values.

It is interesting to observe that the same effect can be observed in Table 51, where for both runs the C in the products is low and the hydrogen high. In this case, more error in feed analysis probably exists, and the missing CO_2 product is much larger. However, even when this is allowed for, the C recovery is still too low. Again, the gain of weight by the char due to oxygen and water adsorption is the probable explanation.

Table 50

Elemental Mass Balances

Devco Bituminous Coal, -149 +74 μm, CO_2, 0.8 s.

As fed, C - 84.37, H - 5.32, S - 1.06, N - 1.68, O - 4.37

Run	Temp. °C		Gas	Tar	Char	Total H_2O	Total
			Gms. of element in product/100 gms. coal as fed				
121	600	C	2.27	12.58	53.30		68.2
		H	0.55	1.10	3.03	1.05	5.73
		Yield	3.06	15.54	65.65	9.41	93.66
120	650	C	3.02	12.40	55.64		71.1
		H	0.80	1.17	2.87	0.84	5.68
		Yield	4.33	15.78	71.20	7.59	98.90
122	700	C	4.03	15.15	49.90		69.1
		H	1.06	1.21	2.34	0.38	4.99
		Yield	6.11	18.76	62.26	3.41	90.54

Table 51

Elemental Mass Balances

Saskatchewan Lignite 3, -149 +74 μm, 0.8 s.
As fed, % C 59.6 H 4.4 N 1.37 O 25.9 Moisture 7.6 Ash 8.8
Temperature 650°C, CO_2 atmosphere

Run		Gas	Tar	Char	Total H_2O	Total
		gms. of element in product / 100 gms. coal fed				
119	C	3.94	5.06	37.22		46.22
	H	0.35	0.49	1.37	3.27	5.48
	Yield	7.60	6.62	60.4	29.40	104.02
124	C	3.97	4.30	42.54		50.81
	H	0.49	0.43	1.55	2.42	4.89
	Yield	7.61	5.93	60.2	21.77	95.51

In future work, to obtain good elemental balances, not only reasonably dry feed should be used, but elemental analyses of products should be carried out as soon as possible, and chars should be stored in dry inert atmospheres with a minimum of exposure to ambient conditions during handling.

CONCLUSIONS

A comparison of maximum liquid yields among Canadian coals of different ranks is shown in Table 52. The maximum hydrocarbon liquid yield (18.4% maf) is obtained from the Eastern Canadian high volatile Devco bituminous coal. There is apparent no general correlation between maf volatiles as determined by proximate analysis and tar yields by flash pyrolysis. However, it is interesting to observe that within the one rank of bituminous coals, the tar yields do increase as the maf volatiles increase. A similar trend does not appear to exist for low rank coals.

As shown in Figure 23, the tar yield from Canadian bituminous (black) coals in flash pyrolysis is just about what would be expected from the CSIRO correlation, which was derived, in the main, for high volatile bituminous coals. Again, it should be remembered that the data given in Table 52, and plotted in Figure 23, have not been adjusted or normalized in any way, but are the direct experimental values. A significant part of the material balance losses is probably due to loss of volatiles, and therefore the results given can be taken to be reasonably conservative.

The maf volatiles reported in Table 1 for two of the coals were determined using a thermogravimetric analysis unit. This procedure is both fast and sufficiently accurate and results for duplicate proximate analyses of the Hat Creek coal are shown in Appendix 1. A detailed sample calculation for Run 56 is given as Appendix 2.

In most cases, the effect of temperature on liquid yield was typical of the fluid bed fast pyrolysis process. An optimum (maximum) yield was observed, usually at 600°-650°C. However, for two bituminous coals, this maximum yield occurred between 650°-700°C. The maximum point tends to be more pronounced for the bituminous coals and less so for the lower rank coals. The H/C atomic ratios of the tar product also show interesting variations with temperature. For all the low rank coals, the H/C ratio of the tar decreases with temperature from about 1.25 to 0.9 over the range of 500°-750°C. However, for the higher rank coals the H/C ratio of the tar is reasonably constant at 0.90 - 1.05 with the lower values corresponding to the lower volatile bituminous coals. The approximate oxygen content does not show any very clear trends with temperature, and varies from 8-16% for low rank coals and 8-10%

for higher rank coals. Although the oxygen content of the raw coals varies widely, the deoxygenation during pyrolysis by the formation of CO, CO_2 and H_2O appears to be much more effective for the low rank coals than it is for bituminous coals.

The H/C atomic ratio of the chars show much the same pattern of behaviour with temperature as do the tars. The H/C ratio in chars for lower rank coals decreases steadily with temperature from about 0.6 - 0.35 over the range of 500°-750°C. However, the H/C ratio of the chars for the bituminous coals remains reasonably constant at 0.55-0.65 except for Devco coal which shows a small decrease with temperature (from 0.57 to 0.39). The H/C ratio indicates to some degree the nature of the material. The tars with H/C ratios of unity or slightly greater, suggest primarily simple single aromatic ring compounds, with more ring substituents, such as cresols, xylenes or phenols, etc., for the lower rank coals and fewer for the higher rank coals. The H/C ratios of the order of 0.5 found in the chars suggest polynuclear aromatic structures containing several ring units.

Residence time cannot be readily varied over wide ranges in a fluidized bed reactor, and two sizes of reactor were required in this work to obtain the range 0.2-1.4 seconds. The residence time effect was investigated in detail for only one low rank coal and one bituminous coal. The shortest time (0.2 or 0.45 seconds respectively) gave the highest tar yields, with the effect being more pronounced with the lower rank coal. However, it should be remembered that the use of very short residence times in fluidized beds requires some further basic investigations to develop adequate reactor scale-up information.

Tests in which the accumulation of char in the bed was measured and compared to tar yields, and tests using a simulated "zero char accumulation" reactor both indicated that the amount of char accumulated in the sand bed had only a minor effect on tar yields. However, work at CSIRO has shown that if the char is heated to 900°-1000°C e.g. in a combustion unit, or if char is used as the heat carrier, then it appears to become activated, and can have a strong negative catalytic effect on tar yields. In the Waterloo process, the char is never heated above the pyrolysis temperature, that is, 650°-700°C, and so would not be activated in this way. Until more is known about these effects, this appears on the basis of existing evidence to be a reasonable explanation of the detrimental effects of char accumulation observed in some work.

The use of a deoxygenation-hydrogenation catalyst (Co-Mo) in place of sand as the fluidized solid with a hydrogen atmosphere in the reactor did not appear to affect product yields for a low rank coal (Hat Creek), but did affect product gas composition, apparently by catalysis of the water gas reaction. For another low rank coal (Forestburg) the catalyst reduced tar yields sharply, and although the tar formed was low in oxygen, this accounted for only a minor part of the yield loss. The product gas again had a composition indicating catalysis of gas phase reactions. It would appear that, at least at atmospheric pressure, this particular catalyst did not have any really beneficial effects during pyrolysis. However, the fact that significant effects were observed, even if not all desirable as in this case, suggests that further investigations with different catalytic materials might yield useful and beneficial results which could offer alternative reaction schemes.

The question of the effect of reaction atmosphere on pyrolytic liquid yields is one which still is not entirely resolved. The use of a hydrogen or methane atmosphere, without catalysis, is fairly predictable, that is, some reduction in tar yields usually occurs with an increase in light hydrocarbon or BTX yield. However, at one atmosphere both of these effects are minor. Work on hydropyrolysis or methanolysis under pressure at other laboratories suggests that much higher pressures and temperatures are required to obtain significant improvement in BTX or light hydrocarbon yields in flash pyrolysis reactors.

The effect of CO_2 (and possibly H_2O) atmospheres on yields of tars is difficult to define with any assurance because of the ability of the raw coal or chars to adsorb strongly considerable amounts of these polar compounds. The conclusion of this work is that CO_2 has little effect on tar yields providing the raw coal feed is fully exposed to a CO_2 atmosphere before pyrolysis. There may be some evidence that fresh unoxidized coal, particularly bituminous coal, may give higher tar yields in CO_2 atmospheres. Further work is needed to verify this possibility. The beneficial effects of CO_2 or H_2O in increasing tar yields reported in the literature appear to be due to the fact that the adsorption of these compounds can de-activate a char which has previously been activated by exposure to high temperatures. Since the Waterloo process does not create chars causing negative effects on tar yields, it is not surprising that little effect of a CO_2 atmosphere was observed.

Quenching of products by the addition of cold gas has been suggested as one means of achieving the effect of a shorter residence time, with its potential benefits. For reasons which are not obvious, quenching in our fluidized reactor did not improve yields of tar; rather tar yields decreased slightly while gas yields increased, although there was no notable change in gas composition. The fluid bed and associated flow system used here had a very small volume and system residence time. Other configurations might benefit from quenching whereas the unit used in this work did not require it to sustain liquid yields. However, quenching also carries the penalty of dilution of condensable products, and the reduction of the quality of the heat available for recovery. Real benefits in yields must therefore result if quenching is to be employed.

Acid washing of low rank brown coals to remove alkaline earth cations associated with organic coal matter has been used with both Australian and U.S. lignites or brown coals to improve the yields of pyrolytic liquids. Acid washing of the Saskatchewan lignite resulted in a dramatic increase in tar yields, by some 40% - 50%. As shown in Table 52, the gas yield also improved, and char yield decreased. The benefits of acid washing appear to be sufficiently great that further investigation is warranted, and this is presently being carried out, not only for the lignite but for other low rank coals as well which might have metallic cations associated with organic matter in the coal. The effect of acid washing on brown coals was shown by Smith, (1981), and his results are reproduced in Figure 25, together with the result obtained with the Saskatchewan lignite. The improvement in tar yield obtained in our work agrees well with what would be expected from the results obtained with other lignites or brown coals. Figure 25 appears to represent a fairly general relationship which should allow prediction of the benefits of acid washing for low rank coals having some ion exchange characteristics.

The use of caking coals in fluidized bed reactors can lead to severe operating difficulties because of caking and agglomeration. Although Australian workers have been able to pyrolyze highly caking coals successfully in fluid beds by using a large sand particle size, we were not able to go to these large sizes in our small bench scale reactor. Similarly, no operating problems have been reported with spouted beds using large sand sizes (small gravel). A Devco bituminous coal was strongly

Table 52

	Estevan Lignite	Forestburg Sub-bit.	Highvale Sub-bit.	Hat Creek Sub-bit.	Devco hvA*	McIntyre Bit.	Balmer Bit.	Sukunka Bit/ Sub-bit.	Estevan Lignite Acid-Washed
Temp. (°C)	650	650	650	650	650	675	650	680	600
Res. Time, s.	0.45	0.45	0.45	0.45	0.80	0.80	0.80	0.50	0.45
Yields wt% maf, at optimum liquid yield									
Gas	14.3	17.9	15.8	20.0	4.4	3.7	3.9	5.7	17.0
Max. Tar**	9.9	9.7	10.7	5.3	17.8	7.0	11.0	13.6	13.7
Char	62.8	58.5	69.1	49.2	67.8	86.9	80.7	78.8	56.0
BTX	0.43	0.4	0.44	0.2	0.6	0.2	0.4	-	0.1
H_2O	6.9	7.0	3.9	-	4.7	3.8	1.9	-	5.9
Total	94.3	93.5	99.9	74.7	95.3	101.6	97.9	98.1	92.7
Tar Atomic H/C	1.14	1.10	1.06	1.22	1.08	0.91	0.92	-	0.86

* Average of two runs
** Tar includes $C_4 \rightarrow C_8$ fraction

pre-oxidized and used as a pyrolysis feed, since this is known to reduce the caking propensity, and this pre-treatment does allow trouble free operation of a conventional fluidized bed. However, tar yields were also sharply reduced by the pre-oxidation. Presumably, some optimum exists between the degree of oxidation, operating problems and tar yields. Further work is probably justified to determine the value of feed pre-oxidation.

Particle size of the coal feed was not varied widely, but indications are that a minimum coal particle size of about 75-100 μm would be desirable for a fluid bed. Maximum particle size is not really known, and would depend on heat transfer limitations. Other work suggests that sizes to 1000 μm might be satisfactory. Although in a practical situation a ground coal feed will contain some fines, it is suggested that coal feed preparation should be such that the production of fines (-75 μm or -200 mesh) should be minimized if a fluidized bed (or probably a spouted bed) is to be used for the pyrolysis reaction.

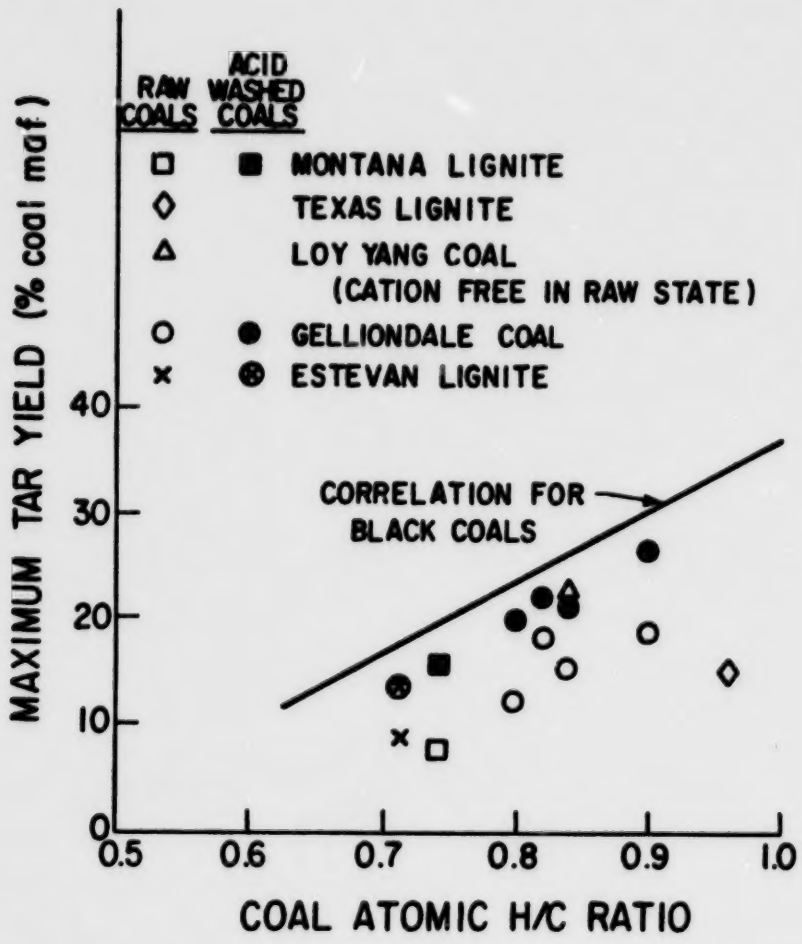

Figure 25 CSIRO Correlation for Maximum Tar Yields from Raw and Acid Washed Low Rank Coals (Smith, 1981) showing present results for Saskatchewan lignite.

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